Draft

CRPAQS Data Analysis Task 2.7
When and Where Does High O_3 Correspond to high $PM_{2.5}$?
How Much $PM_{2.5}$ Corresponds to Photochemical End Products?

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Executive Summary

Two questions are addressed in California Regional PM Air Quality Study (CRPAQS) data analysis Task 2.7: (1) Where and when do elevated ozone concentrations correspond to excessive $PM_{2.5}$ concentrations? (2) What fraction of $PM_{2.5}$ corresponds to photochemical end products? We address these questions using hourly and other continuous data for Angiola, Bakersfield, and Fresno.

E.1 High O_3 vs. High $PM_{2.5}$

On an annual basis, O_3 and $PM_{2.5}$ do not correlate. Any relationship is obscured by the seasonal behavior of these pollutants, i.e., O_3 being high in the summer and $PM_{2.5}$ being high in the winter. When the dataset is stratified by season, seasonal and geographical differences in the relationship between O_3 and $PM_{2.5}$ are revealed.

- In Angiola, the rural site, top 20^{th} percentile O_3 and $PM_{2.5}$ concentrations occur simultaneously most frequently in winter
- In Bakersfield and Fresno, top 20^{th} percentile O_3 and $PM_{2.5}$ concentrations occur simultaneously most frequently in summer

O_3 and $PM_{2.5}$ show very different diurnal behaviors. The 24-hour cycle of O_3 is very pronounced in both the winter and summer time series at all three locations. O_3 is removed every evening by chemical titration and builds up from a low concentration in the early morning. $PM_{2.5}$ fluctuations show no discernable cycles in the summer. During winter, $PM_{2.5}$ shows a lot of structure: daily cycles are seen on some days to superimpose on a longer term build-up. However, there is no consistent shape to the diurnal cycle of $PM_{2.5}$ as there is for O_3. $PM_{2.5}$ does not show a consistent removal process. While PM concentrations decrease during some hours of the day, long-term accumulation is observed during winter episodes.

During winter, high concentrations of $PM_{2.5}$ and O_3 occur together in Angiola because daily peak concentrations for both species occur during the day on many days with high PM concentrations. The diurnal cycles of winter PM and O_3 at the urban sites show a phase difference between these two pollutants.

In Angiola, nitrate is the dominant component of winter $PM_{2.5}$ and the daytime peaks of $PM_{2.5}$ are caused by daytime peaks in $PM_{2.5}$ nitrate concentrations. Since daytime conditions are comparatively less favorable for nitrate to partition into the particulate phase, peak concentrations during the 1 to 4 p.m. period are strongly indicative of a daytime chemical process occurring at this site. Nighttime drops in nitrate concentrations may be due to removal by fog. There is some indication of nitrate formation aloft, but the contribution of aloft nitrate to surface observations at this site is not readily observed as a consistent morning increase of surface nitrate is lacking in the Angiola data.

The difference in the nitrate diurnal profiles in Angiola and at the urban sites indicates that the dominant processes contributing to the observed surface nitrate concentrations

may be different at urban and rural sites. Transport from aloft was assumed by Watson and Chow (2004) to account for a morning increase in nitrate concentrations at the Fresno supersite. A more complete understanding of the formation of nitrate at various locations awaits reliable and simultaneous measurements of NO_2, HNO_3 (maybe NO_3 radicals) and particulate nitrate.

In Fresno, organic compounds dominate the $PM_{2.5}$ concentrations in winter. Organic compounds concentrations peak at night, coincidental with $PM_{2.5}$ mass concentrations. Since organic compounds are more concentrated around urban areas than rural areas, it is inferred that urban-scale nighttime emissions, e.g., from residential wood burning, are a major source of organic compounds in urban areas.

During summer, high concentrations of $PM_{2.5}$ and O_3 occur together in Fresno and Bakersfield because there is a stronger tendency for O_3 and $PM_{2.5}$ to build up together during an episode. The long-term trends, calculated using 24-hour average $PM_{2.5}$ and daily maximum 8-hour average O_3 concentrations, show stronger correlations at the urban sites than at the rural site.

E.2 Contribution of Photochemical End Products to $PM_{2.5}$

Secondary compounds that are produced from photochemical reactions include ammonium nitrate, ammonium sulfate, and a portion of the organic compounds. The estimated average concentrations of ammonium nitrate, sulfate, and secondary organic carbon (SOC) for the rural and urban sites are listed in Table E-1 for the winter season. The estimates of SOC are based on the OC/EC method, with a site-specific minimum OC/EC ratio that is calculated to represent the source mixture at each site, because urban sites are postulated to be affected by local, rather than regional, emissions. The primary ratio is estimated to be 13% higher in Fresno than in Bakersfield. There is some evidence that the contribution of primary organic carbon (POC) in Angiola is higher on exceedance days.

Photochemical end products account for more than half of $PM_{2.5}$ in Angiola and Bakersfield but for less than half of $PM_{2.5}$ in Fresno.

Table E-1. Concentration ($\mu g/m^3$) of ammonium nitrate, ammonium sulfate, and secondary organic carbon during winter at Angiola, Bakersfield, and Fresno.

Compound	Angiola	Bakersfield	Fresno
Ammonium nitrate	26.9	30.7	23.1
Ammonium sulfate	2.3	3.1	2.1
Secondary OC	2.1	2.4	2.8
$PM_{2.5}$	56.3	58.9	67.3

1. Introduction

Two questions are addressed in California Regional PM Air Quality Study (CRPAQS) data analysis Task 2.7: (1) Where and when do elevated ozone concentrations correspond to excessive $PM_{2.5}$ concentrations? (2) What fraction of $PM_{2.5}$ corresponds to photochemical end products?

To address these questions, we obtained data of $PM_{2.5}$ and $PM_{2.5}$ components from the CRPAQS database located on the web at http://www.arb.ca.gov/airways/Datamaintenance/default.asp. Our analyses focus on three main core sites, Angiola, Bakersfield (California Street) and Fresno (First Street). Continuous measurements taken during CRPAQS provide an opportunity to understand the detailed temporal behavior of PM and its components during the winter of 2000 to 2001. We downloaded the following data from the database: (1) $PM_{2.5}$ mass data taken with Beta Attenuation Monitor (method code MASS_PAR_PU0000002500_BAM_BTD_HD_H1), (2) co-located O_3 data, (3) continuous nitrate data (NO3_SOL_PU0000002500_CN3_FLV_AT6_A1H and NO3_SOL_PU0000002500_SFS_ICH_ICG_QTZ_E5_VA), and (4) continous OC and EC data (C_ORG_PU0000002500_SFS_CAA_TOR_NAC_E5_VA and C_ELE_PU0000002500_SFS_CAA_TOR_NAC_E5_VA). Continuous nitrate and O_3 data are available aloft at 100 m at the ANGI location. In addition, 24-hour PM composition data were obtained from CARB for the entire CRPAQS annual study (K. Turkiewicz, personal communication, December 2004).

Section 2 of this report provides a statistical overview of the O_3-PM relationship. The seasonal relationships between O_3 and PM are analyzed further in Section 3. In Section 4, we analyze the behavior of two key secondary PM components, nitrate and organic compounds. In Section 5, we summarize our findings and suggest additional measurements that could be useful in shedding additional light on the formation of secondary compounds.

2. Statistical Analysis of Ozone and $PM_{2.5}$

To determine when and where high ozone and $PM_{2.5}$ correspond, continuous data from three core sites, Angiola, Bakersfield (California Street) and Fresno (First Street) are used. $PM_{2.5}$ and O_3 data are processed to select co-located and simultaneous data for the statistical analyses. For each site, high O_3 and high PM are defined to be the top 20^{th} percentile concentrations. Among these three sites, the highest O_3 concentrations are recorded in Bakersfield. The highest $PM_{2.5}$ concentrations are recorded in Fresno.

As shown in Figures 1 through 3, the relationships between ozone and PM concentrations vary by season. The highest O_3 concentrations are recorded in summer, less frequently in spring and fall; while the highest $PM_{2.5}$ concentrations are recorded in winter, followed by fall. Therefore, on an annual basis, high O_3 and $PM_{2.5}$ do not occur frequently together. Statistical summaries of the O_3 and $PM_{2.5}$ data are presented in Tables 1 to 3 for the three core sites considered. In one year, the number of hourly samples associated with top 20^{th} percentile ozone and $PM_{2.5}$ range from 68 (0.8%) in Fresno and 70 (1.0%) in Bakersfield to 109 (1.6%) in Angiola. Given a 1-hour sample with top 20^{th} percentile O_3 (or $PM_{2.5}$) concentration, there is a low probability (4% in Fresno, 5% in Bakersfield, 8% at Angiola) that the same sample is also associated with top 20^{th} percentile $PM_{2.5}$ (or O_3) concentration.

Because of the differences in the O_3-$PM_{2.5}$ relationships during different seasons, the occurrences of O_3 and $PM_{2.5}$ simultaneously above the respective 80^{th} percentile are noted in Tables 1 to 3 for each season. Within each season, there was a higher probability for high O_3 and $PM_{2.5}$ to occur together. For the urban area of Bakersfield, concurrent O_3 and $PM_{2.5}$ concentrations that are above the respective 80^{th} percentile are recorded during 4% of the spring hours, 5% of the summer hours, 2% of the fall hours, and 3% of the winter hours. For Fresno, the corresponding percentages are 5%, 6%, 1%, and 2% for the four seasons. For Angiola, the number of winter samples with high simultaneous O_3 and $PM_{2.5}$ is notably higher (6%) than for the urban areas. There is also a stronger tendency for high concentrations O_3 and $PM_{2.5}$ to occur together in spring (6% of the samples) and fall (3%). But concurrent high O_3 and high $PM_{2.5}$ seem to occur in summer at about the same frequency as in Bakersfield and less frequently than in Fresno.

Angiola showed different seasonal patterns than Fresno and Bakersfield. In Angiola, relatively higher concurrent O_3 and $PM_{2.5}$ occurred more frequently in winter and in spring, followed by summer, and concurrent high concentrations occur least frequently in fall. In Bakersfield and Fresno, higher concurrent O_3 and $PM_{2.5}$ occurred more frequently in summer than spring and winter, and least frequently in fall. The winter-summer difference between the urban and rural areas will be investigated later.

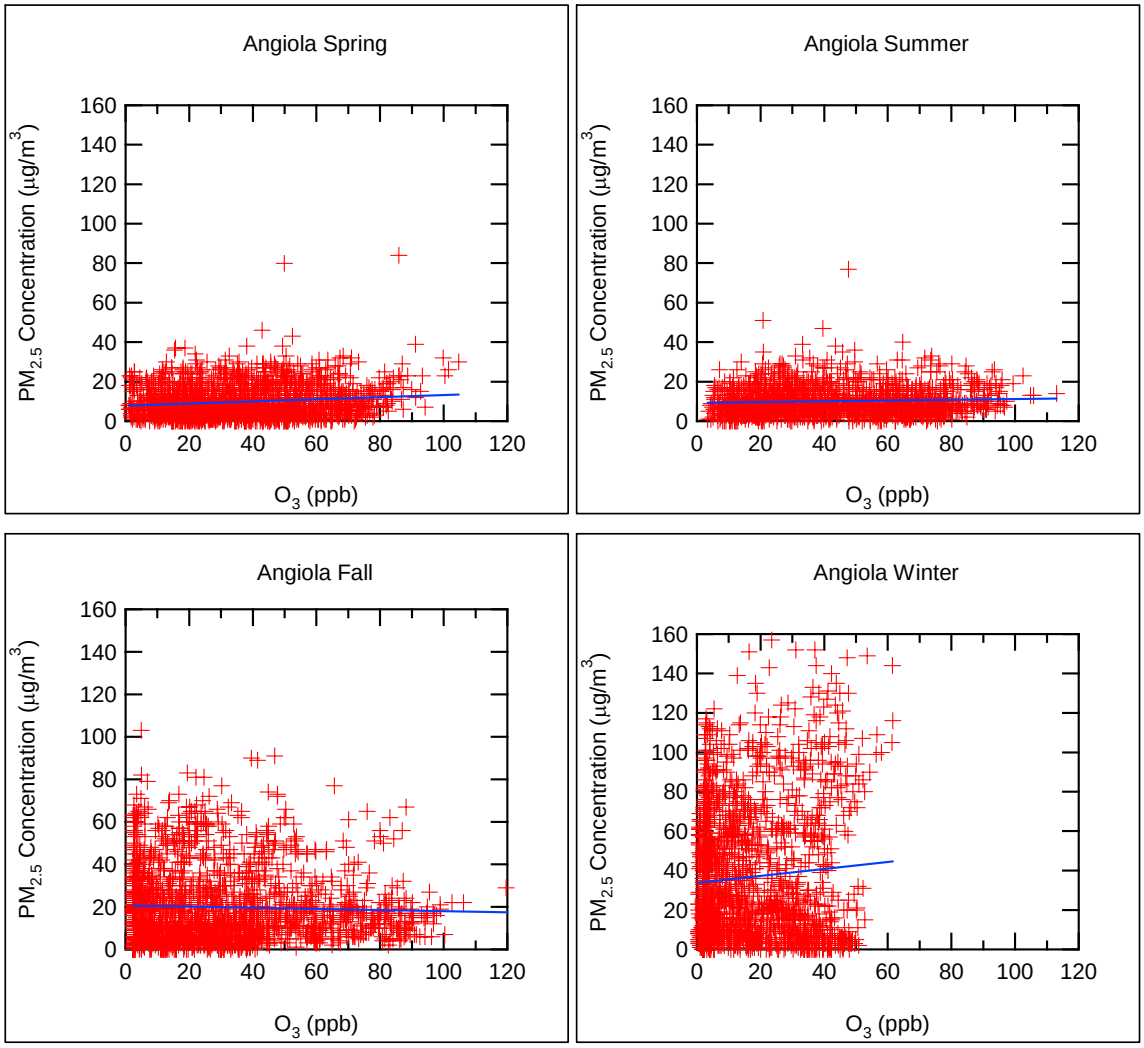


Figure 1. Scatter diagram of hourly $PM_{2.5}$ vs. O_3 concentrations in Angiola

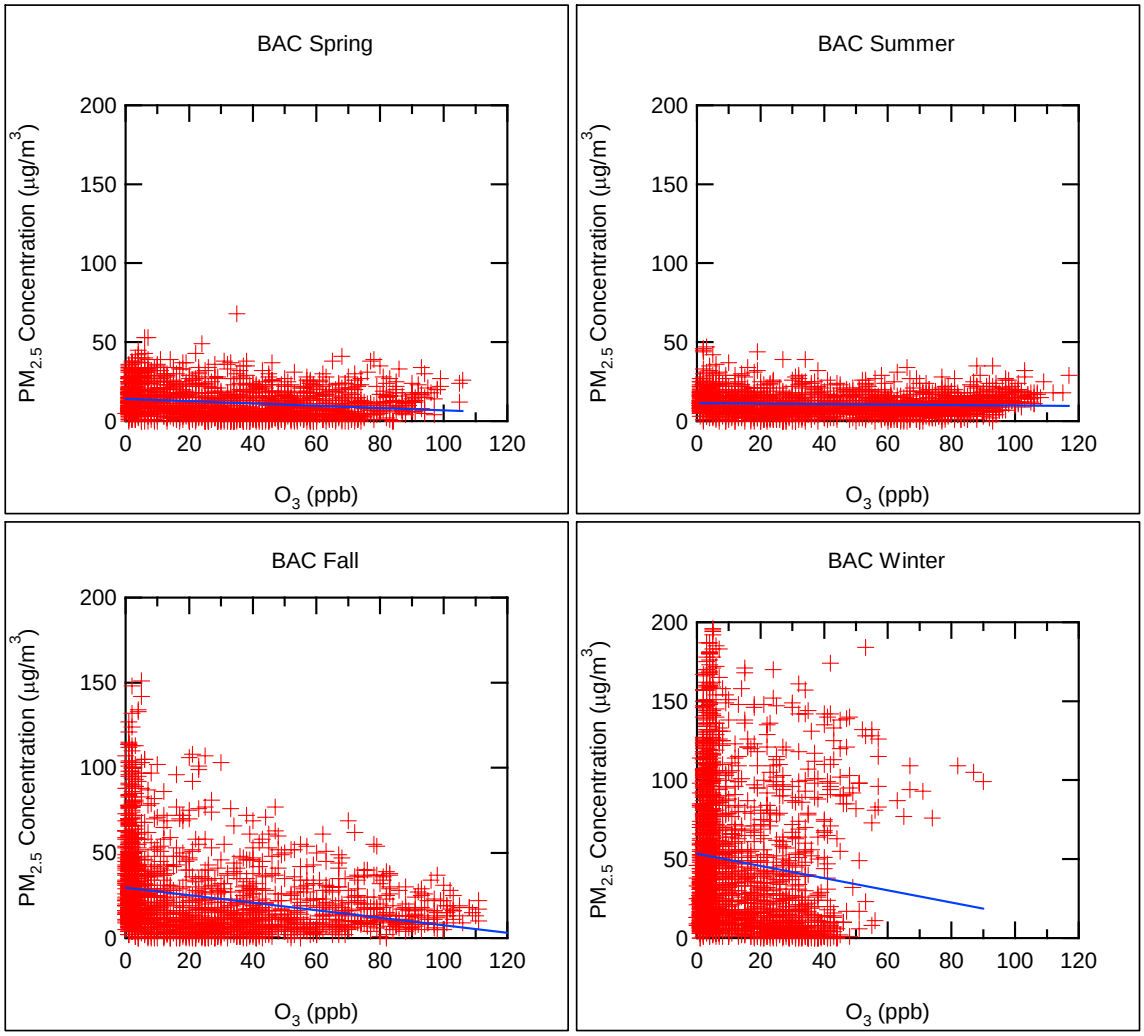


Figure 2. Scatter diagram of hourly $PM_{2.5}$ vs. O_3 concentrations in Bakersfield

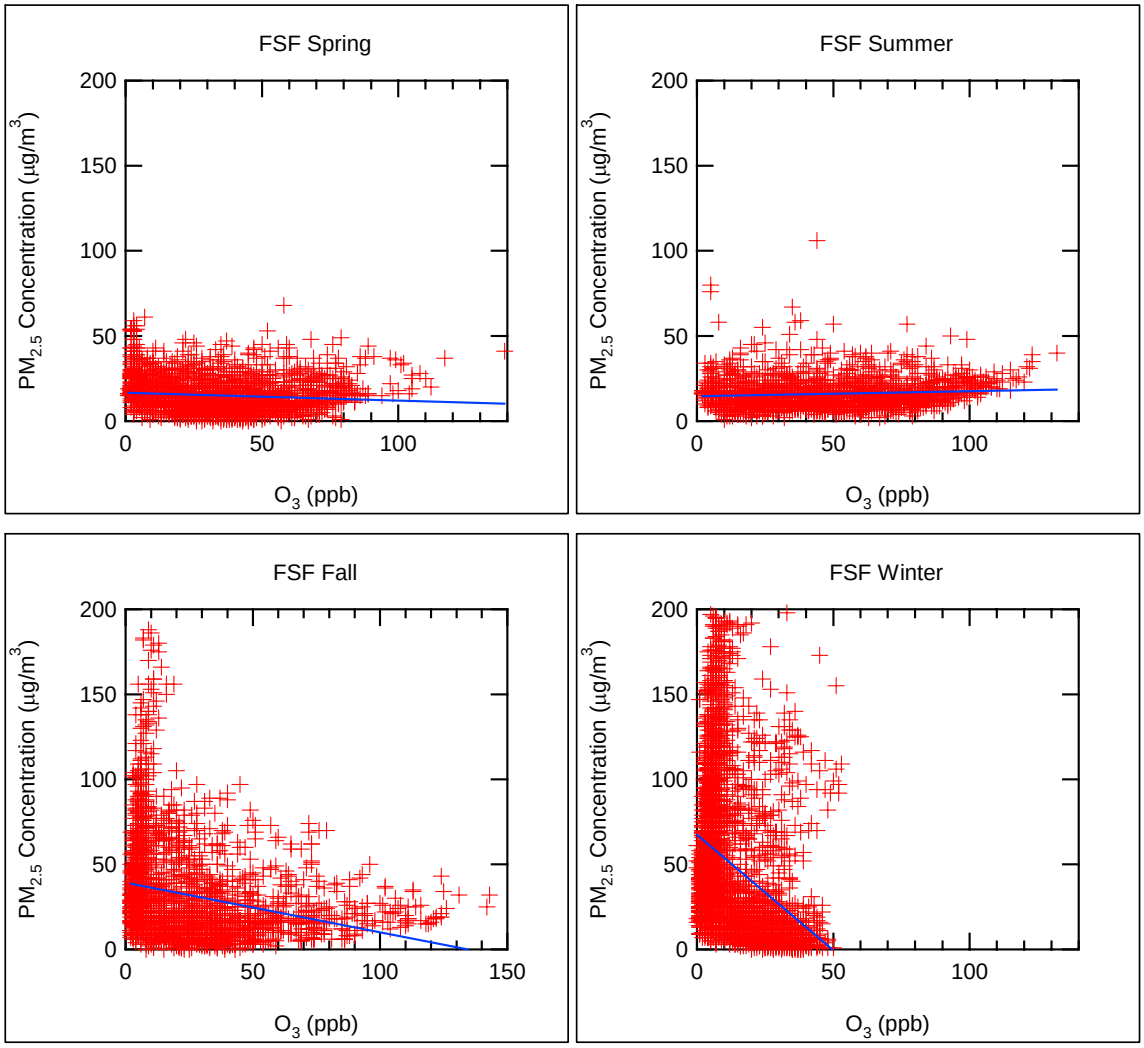


Figure 3. Scatter diagram of hourly $PM_{2.5}$ vs. O_3 concentrations in Fresno

Table 1. Statistical summaries of annual and seasonal O_3 and PM data for Angiola*

	Annual	Spring	Summer	Fall	Winter
80^{th} percentile O_3 concentration (ppb)	51	54	66	50	32
80^{th} percentile PM concentrations ($\mu g/m^3$)	27	16	15	32	66
Total no. of samples	6717	1766	1565	1744	1639
No. of samples with high(1) O_3 and high(1) PM(2)	109 (1.6%)	99 (5.6%)	75 (4.8%)	47 (2.7%)	98 (6.0%)
Conditional probability(3)	0.08	0.28	0.24	0.13	0.30

* Data from February 2000 to January 2001

(1) defined here as the top 20^{th} percentile

(2) if all samples with high O_3 were also associated with high $PM_{2.5}$, the percentage would be 20%

(3) P(high O_3 and high $PM_{2.5}$ | high O_3) = P(high O_3 and high PM | high $PM_{2.5}$)

Table 2. Statistical summaries of annual and seasonal O_3 and PM data for Bakersfield*

	Annual	Spring	Summer	Fall	Winter
80^{th} percentile O_3 concentration (ppb)	57	57	76	45	23
80^{th} percentile PM concentrations ($\mu g/m^3$)	29	19	16	38	67
Total no. of samples	7080	1753	1982	1942	1368
No. of samples with high(1) O_3 and high(1) PM(2)	70 (1.0%)	63 (3.6%)	98 (4.9%)	34 (1.8%)	39 (2.9%)
Conditional probability(3)	0.05	0.18	0.25	0.09	0.14

* Data from January 2000 to December 2000

(1) defined here as the top 20^{th} percentile

(2) if all samples with high O_3 were also associated with high $PM_{2.5}$, the percentage would be 20%

(3) P(high O_3 and high $PM_{2.5}$ | high O_3) = P(high O_3 and high PM | high $PM_{2.5}$)

Table 3. Statistical summaries of annual and seasonal O_3 and PM data for Fresno*

	Annual	Spring	Summer	Fall	Winter
80^{th} percentile O_3 concentration (ppb)	50	52	74	41	24
80^{th} percentile PM concentrations ($\mu g/m^3$)	39	22	21	50	77
Total no. of samples	8028	2112	1817	2081	2018
No. of samples with high(1) O_3 and high(1) PM(2)	68 (0.8%)	102 (4.8%)	113 (6.2%)	28 (1.3%)	36 (1.8%)
Conditional probability(3)	0.04	0.24	0.31	0.07	0.09

* Data from January 2000 to December 2000

(1) defined here as the top 20^{th} percentile

(2) if all samples with high O_3 were also associated with high $PM_{2.5}$, the percentage would be 20%

(3) P(high O_3 and high $PM_{2.5}$ | high O_3) = P(high O_3 and high PM | high $PM_{2.5}$)

3. Seasonal Differences and Urban-Rural Differences in the $PM_{2.5}$-O_3 Relationships

From Figures 1 through 3, the relationship between O_3 and $PM_{2.5}$ concentrations in summer is significantly different from that in winter at each of the three sites. During summer, $PM_{2.5}$ concentrations are typically low compared to winter values; and top 20^{th} percentile $PM_{2.5}$ concentrations can be associated with different concurrent O_3 concentrations at all three sites.

During winter, many high PM concentration measurements are related to low O_3 measurements at all three sites, and many relatively higher O_3 measurements are associated with lower $PM_{2.5}$ concentrations, resulting in a dense distribution of data points within a right angle triangle next to the origin of the scatter plots. The data points with concurrent $PM_{2.5}$ and O_3 concentrations are the exceptions. In Angiola, there are enough such data points to result in an overall positive correlation between $PM_{2.5}$ and O_3 in the winter scatter plot. The lower occurrence of relatively high PM associated with relatively high O_3 at the urban sites result in an overall negative trend in winter.

We investigate the seasonal relationships in greater detail below.

3.1 Summer

The top panel of Figure 4 shows the O_3 and $PM_{2.5}$ time series for a period between June 17 to July 7, 2000 for Angiola. The continuous diurnal profile of O_3 is dominated by a strong diurnal cycle, whereas the $PM_{2.5}$ data show no discernable diurnal or periodic signal in the summer time. Daytime peaks are visible on some days, but other days show nighttime peak concentrations. An average diurnal profile is calculated using the available data for the period of June through August 2000, and grouping them by the hour of day. The average concentration for each hour is calculated to generate the average diurnal profile shown in the middle panel for O_3 and $PM_{2.5}$. The daily O_3 peak is emphasized in this profile to occur at about 2 p.m. The diurnal variability in $PM_{2.5}$ is much weaker with no discernable daytime peak. The bottom panel of Figure 4 shows the frequency distribution of concentrations in the top 20^{th} percentile by the hour of day. High O_3 concentrations occur during daylight hours, most frequently in the mid to late afternoon. Top 20^{th} percentile $PM_{2.5}$ concentrations can occur at any hour of the day, although they show the highest frequencies in early morning (6-7 a.m.) or in the evening (after 5 p.m.). As a result, concurrent high concentrations of O_3 and $PM_{2.5}$ are recorded only infrequently during summer in Angiola.

Figure 5 presents the time series and diurnal variation for Bakersfield. The $PM_{2.5}$ and O_3 characteristics in Bakersfield are very similar to those in Angiola. High $PM_{2.5}$ concentrations occur a little more frequently in the afternoon and a little less frequently in the early evening in Bakersfield compared to Angiola.

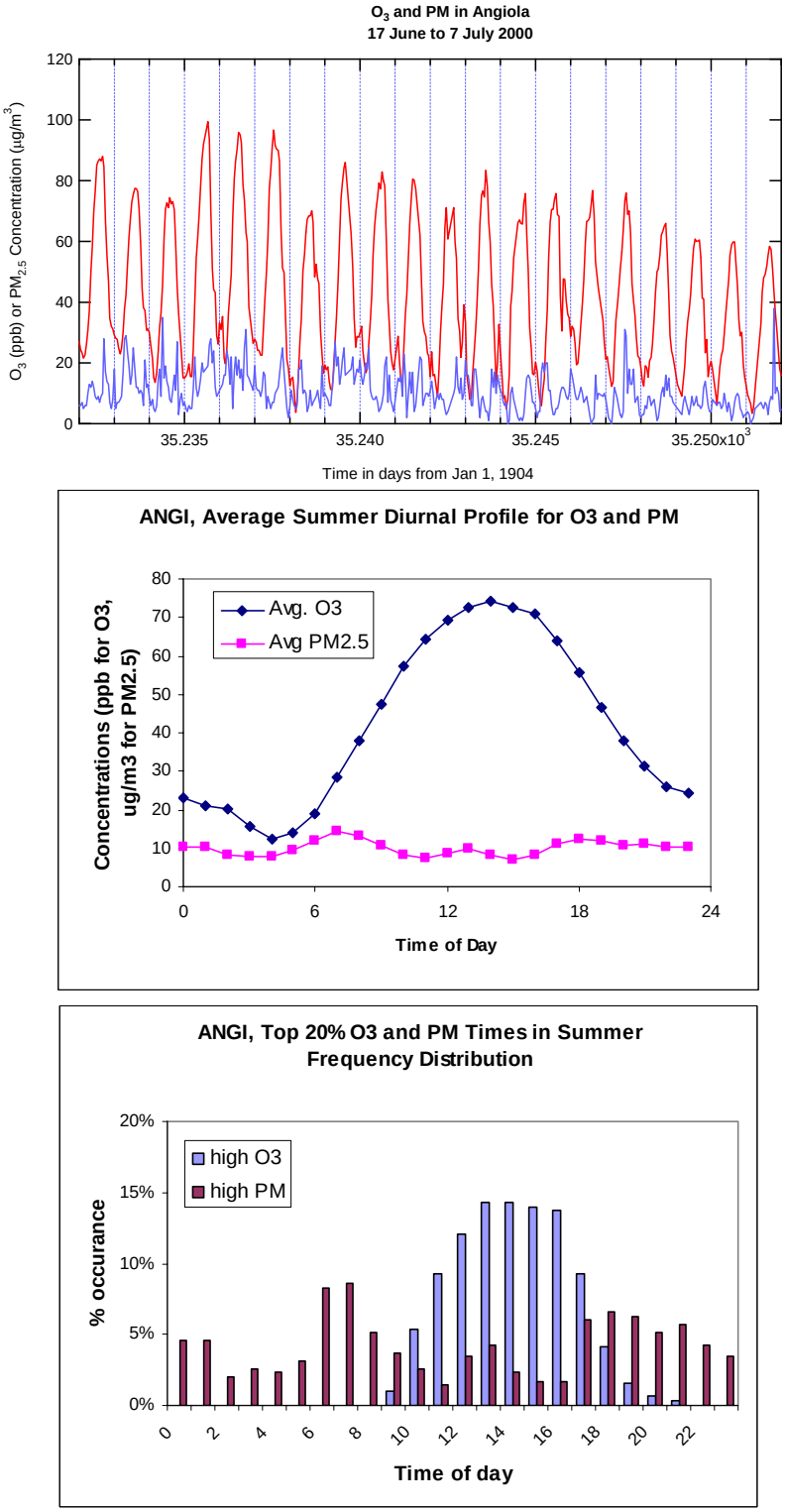


Figure 4. $PM_{2.5}$ and O_3 in Angiola during summer: (top) time series between 17 June and 7 July 2000, (middle) average summer diurnal profiles, and (bottom) frequency distribution by hour of top 20th percentile concentrations.

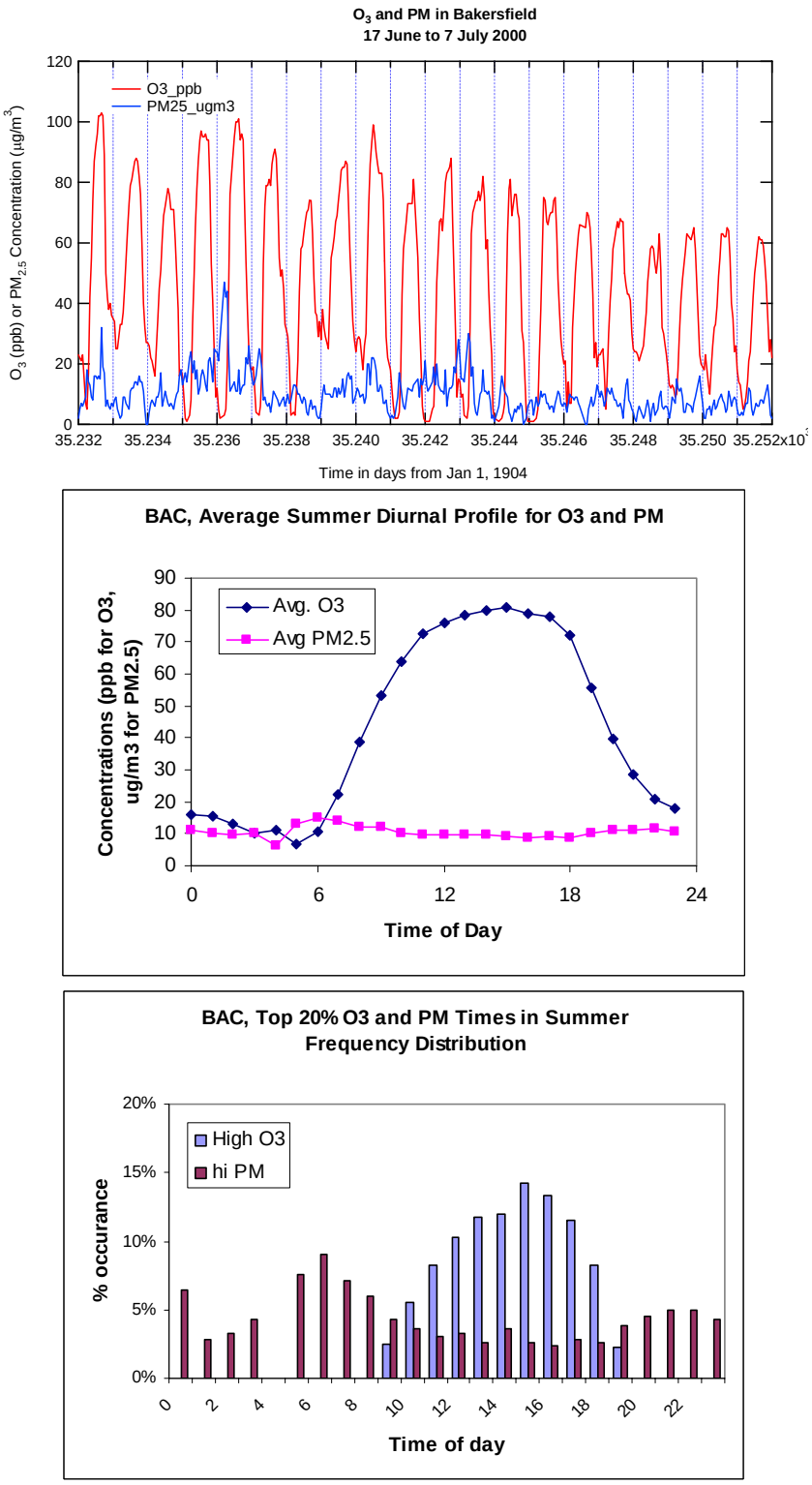


Figure 5. $PM_{2.5}$ and O_3 in Bakersfield during summer: (top) time series between 17 June and 7 July 2000, (middle) average summer diurnal profiles, and (bottom) frequency distribution by hour of top 20th percentile concentrations.

Figure 6 presents the time series and diurnal variation for Fresno. The time series plot shows strong O_3 variations. On a few days, $PM_{2.5}$ accumulates during the morning hours and shows a midday peak. The daytime peak is not visible in the average diurnal profile, but the occurrence of top 20^{th} percentile PM concentrations in the morning on some days is reflected in the frequency distribution. Due to the greater overlap between the hours with high O_3 and high $PM_{2.5}$, at least on some days, there is a greater number of hours with high concurrent O_3 and $PM_{2.5}$ in Fresno than at the other two sites.

While there seems to be little correlation between O_3 and $PM_{2.5}$ on an hourly basis or even an episode basis, some covariance is evident for the summer season when one inspects the seasonal variability of these two species. Figure 7 shows O_3 and $PM_{2.5}$ as a function of time for the three months of June through August 2000 for Bakersfield. Several coincidental periods of high concentrations are observed for O_3 and $PM_{2.5}$; for example on June 15, 21, 27, July 14, 28, August 2, 17, and 25. This type of correlation is also seen in the data for Angiola and Fresno; those data sets have larger gaps compared to that for Bakersfield and are not shown. The O_3-$PM_{2.5}$ relationship was not teased out in the analysis of the time series data because of the phase difference in the O_3 and $PM_{2.5}$ diurnal cycle, as shown in Figures 3b, 4b, and 5b. To study the daily variability, we calculate the 8-hour average O_3 concentrations between 10 a.m. and 6 p.m., which usually represent the daily maximum 8-hour average O_3 concentrations, and the 24-hour average $PM_{2.5}$ concentrations.

Figure 8 displays the daily maximum 8-hour average O_3 and 24-hour average $PM_{2.5}$ concentrations for the summer 2000 period. The spatial variability in the maximum 8-hour concentration of O_3 on any given day is small among the core sites in Angiola, Bakersfield, and Fresno. The low spatial variability is consistent with a regional distribution of summer O_3 due to efficient transport aloft. On any given day, Bakersfield or Fresno is likely to have higher concentrations than Angiola, which may be an indication of local production of O_3 from urban emissions at these locations, which supplement the regional concentrations. Fresno also shows lower concentrations than the rural site on some days, especially when the afternoon peak O_3 concentrations are low. The lower concentrations may be a result of titration by NO emitted in the urban area.

The variability of $PM_{2.5}$ among the same three areas is higher, considering the 24-hour average metric being used here. The difference in concentrations lies mostly with Fresno showing higher $PM_{2.5}$ than Bakersfield and Angiola. On an absolute basis, high 8-hour average O_3 and 24-hour average PM are more likely to occur in Fresno than in Angiola or Bakersfield. The correlation coefficients between 24-hour average $PM_{2.5}$ and daily maximum 8-hour average O_3 are 0.58 at Angiola, 0.68 at Bakersfield, and 0.65 at Fresno, implying that high average O_3 and average $PM_{2.5}$ are more likely to simultaneously occur in the urban areas than in the rural area.

Higher likelihood of high 24-hour average $PM_{2.5}$ and 8-hour average O_3 concentrations in Bakersfield and Fresno indicates that synoptic conditions that favor the regional build up of O_3 lead to increased local influence on $PM_{2.5}$. These conditions may include reduced

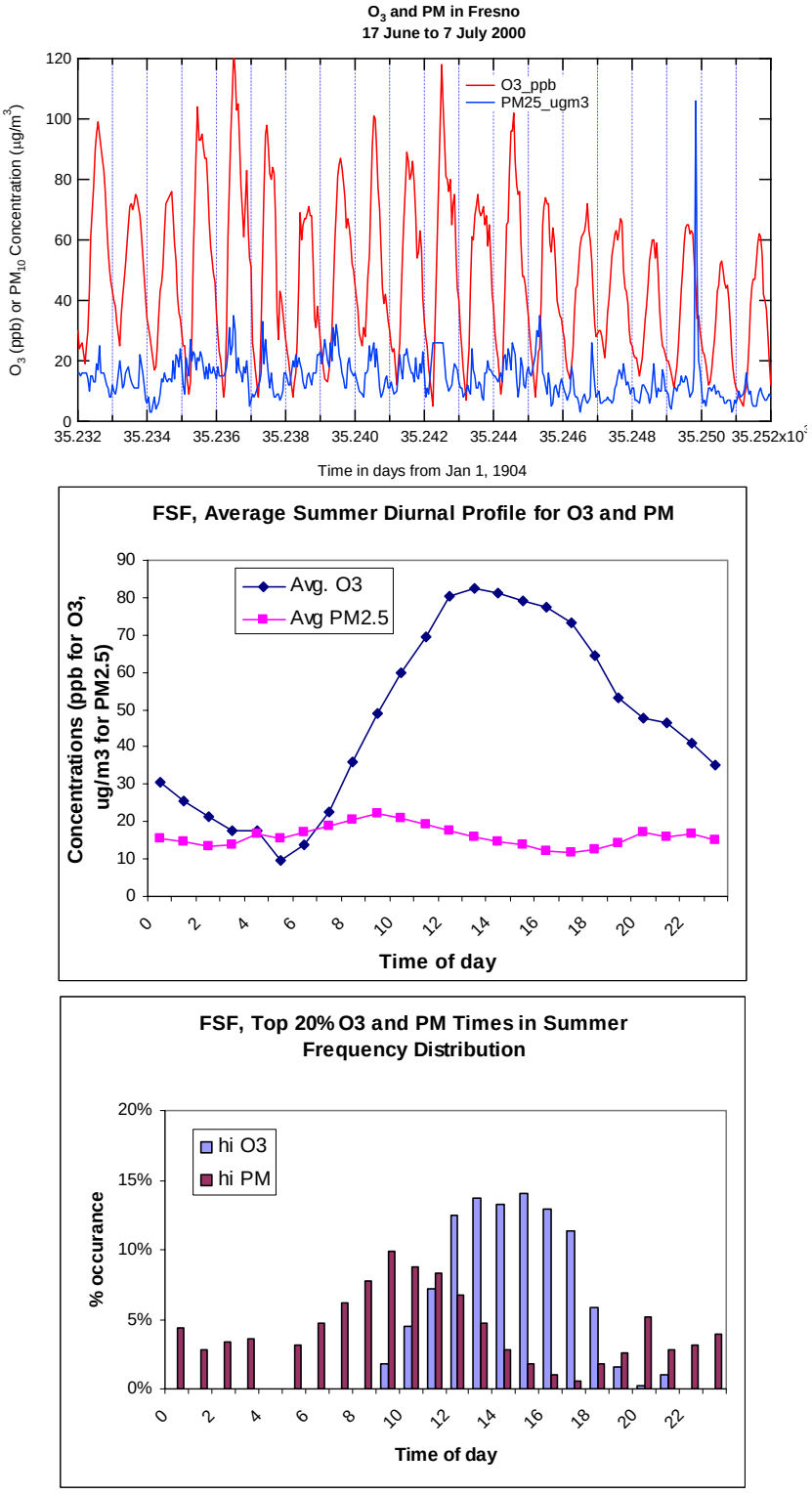


Figure 6. $PM_{2.5}$ and O_3 in Fresno during summer: (top) time series between 17 June and 7 July 2000, (middle) average summer diurnal profiles, and (bottom) frequency distribution by hour of top 20th percentile concentrations.

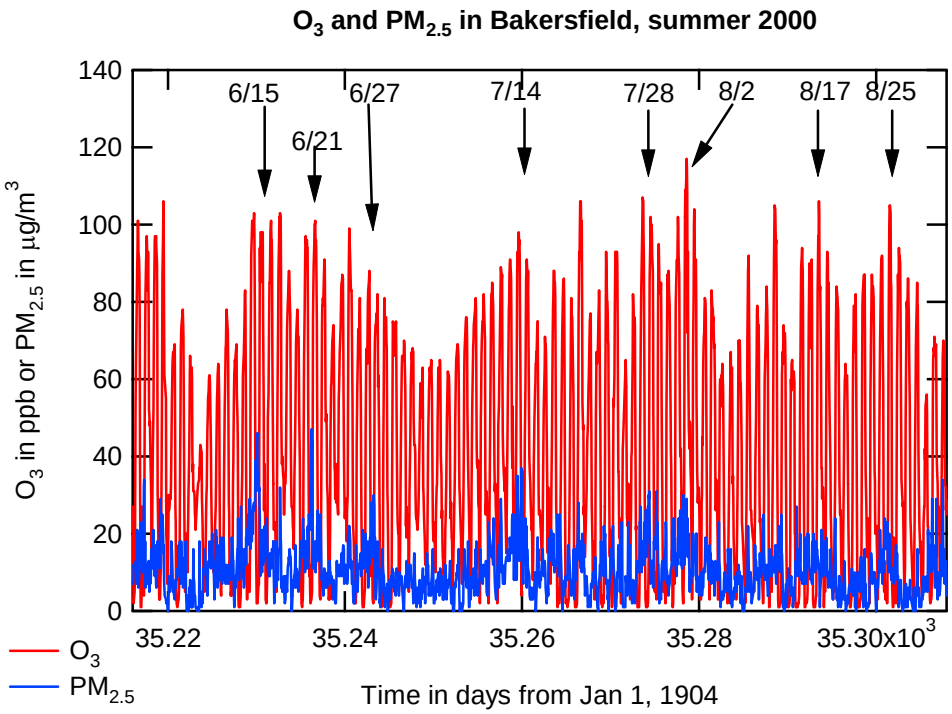


Figure 7. $PM_{2.5}$ and O_3 time series between June and August 2000 in Bakersfield.

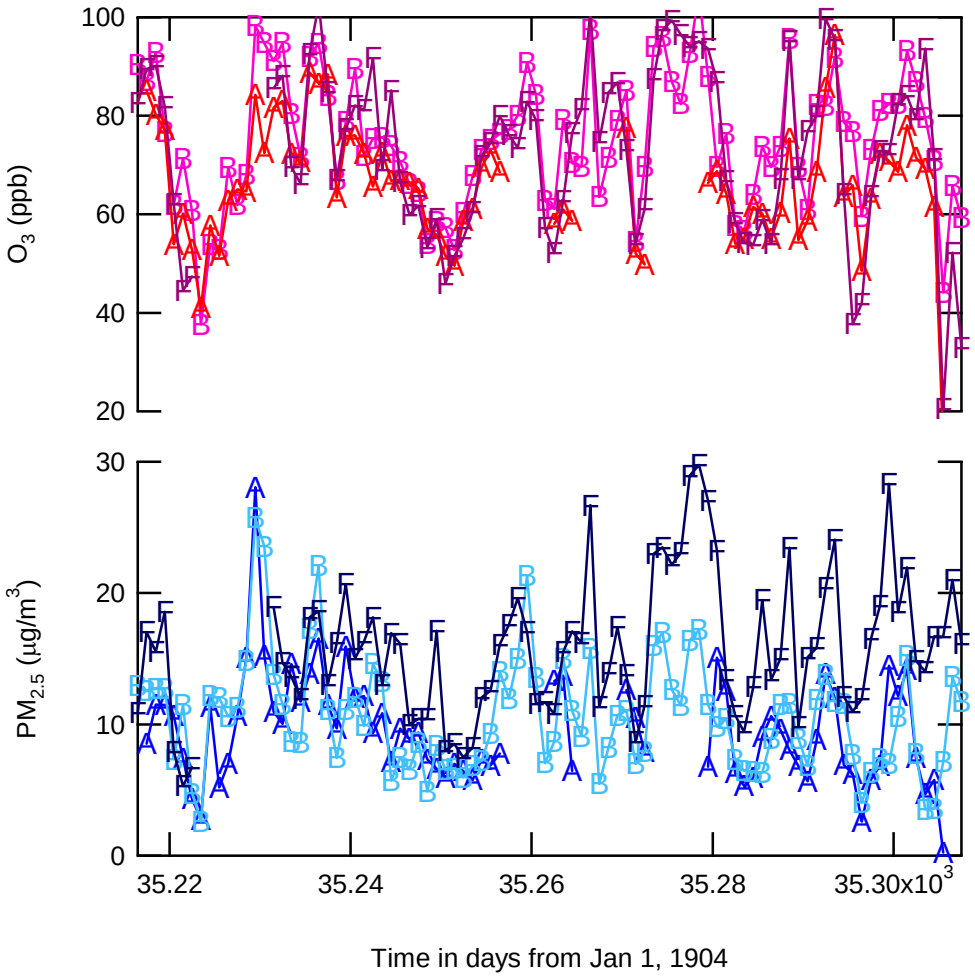


Figure 8. Daily 24-hour average $PM_{2.5}$ and maximum 8-hour average O_3 time series between June and August 2000 in Angiola (A), Bakersfield (B) and Fresno (F).

mixing and a build-up of urban scale primary emissions of $PM_{2.5}$ or increased photochemistry of secondary PM precursors that are more abundant in urban areas than rural areas. The lack of correlation between hourly concentrations of O_3 and $PM_{2.5}$ indicates that the role of O_3 as a limiting oxidant precursor of secondary $PM_{2.5}$ components is likely to be small in the summer.

3.2 Winter

The top panel of Figure 9 shows the time series of O_3 and $PM_{2.5}$ concentrations during a $PM_{2.5}$ episode in Angiola. Compared to the summer time series in Figure 4, O_3 concentrations are much lower, with daytime peak concentrations around 50 ppb. $PM_{2.5}$ concentrations, on the other hand, are much higher than typical summer values. A notable difference between the summer and winter time series plots is that during the wintertime episode, there were many days when peak PM concentrations occur during the day. The average diurnal profile of PM (Figure 9, middle panel) shows a broad daytime peak for $PM_{2.5}$ and a narrower peak for O_3. Because of the tendency for high PM to occur during the day in the winter time, there is more significant overlap in winter between the time of day when high O_3 occurred and when high $PM_{2.5}$ occurred. Therefore, considering hourly concentrations in Angiola, the probability that high O_3 and $PM_{2.5}$ would occur together is higher than in winter than in summer.

There are two possibilities for the PM daytime peak. First, a daytime production process is responsible for the increase in PM mass. Second, high concentrations of PM (and O_3) are mixed in from aloft where these pollutants are higher in concentration because they are transported from a source area, produced, or simply not depleted. The second scenario could explain the seemingly simultaneous accumulation of these species in the morning in Angiola. O_3 is typically higher aloft at night (see Figure 10), because the aloft layer is isolated from the surface layer, where O_3 is titrated away by emissions of NO throughout the night. To investigate the effects of mixing from aloft on surface $PM_{2.5}$, aloft measurements of $PM_{2.5}$ data would be needed. There is no $PM_{2.5}$ mass measurement taken on the tower platforms above 100 m to support this investigation. We will investigate the two possibilities in Section 4 for the nitrate component.

The diurnal profiles provide some evidence of an effective $PM_{2.5}$ removal process at night. Since horizontal and vertical transport are typically limited, the removal process responsible for the decrease in $PM_{2.5}$ concentrations during many evenings is likely to be deposition. $PM_{2.5}$ is not effectively removed by dry deposition, which is likely to be more significant during the day than at night because the stable atmospheric conditions at night limit diffusion to the surface. The other possibility is wet removal by fog droplet. This process is particularly important for nitrate, because both nitrate and the gas-phase precursor HNO_3, can be efficiently removed in even a shallow fog (J. Collett, personal communication, December 2005). If HNO_3 is removed from the gas-phase, some particulate nitrate may evaporate from the particles due to phase equilibrium driving forces.

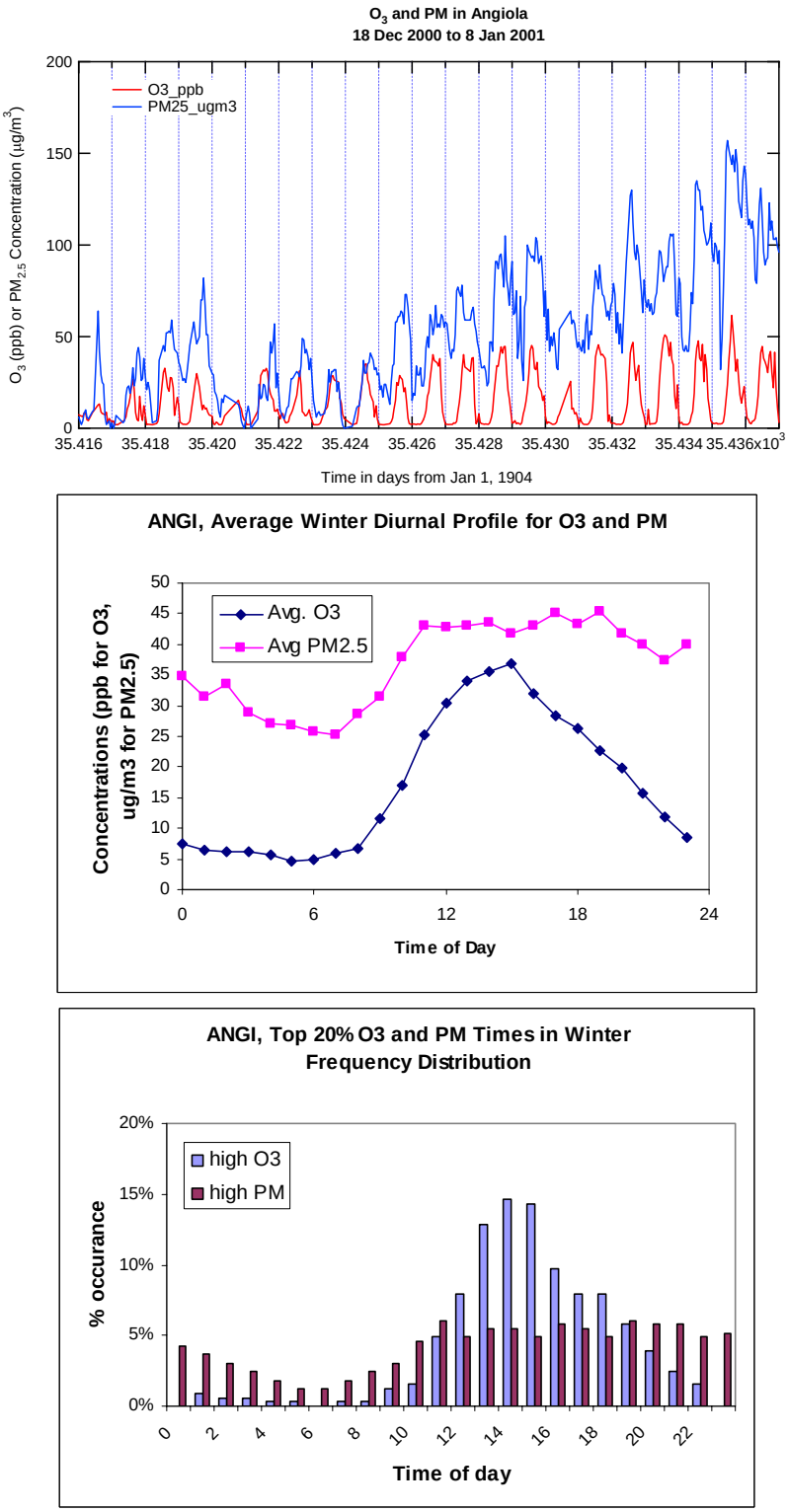


Figure 9. $PM_{2.5}$ and O_3 in Angiola during winter: (top) time series between 18 December 2000 and 8 January 2001, (middle) average winter diurnal profiles, and (bottom) frequency distribution by hour of top 20th percentile concentrations.

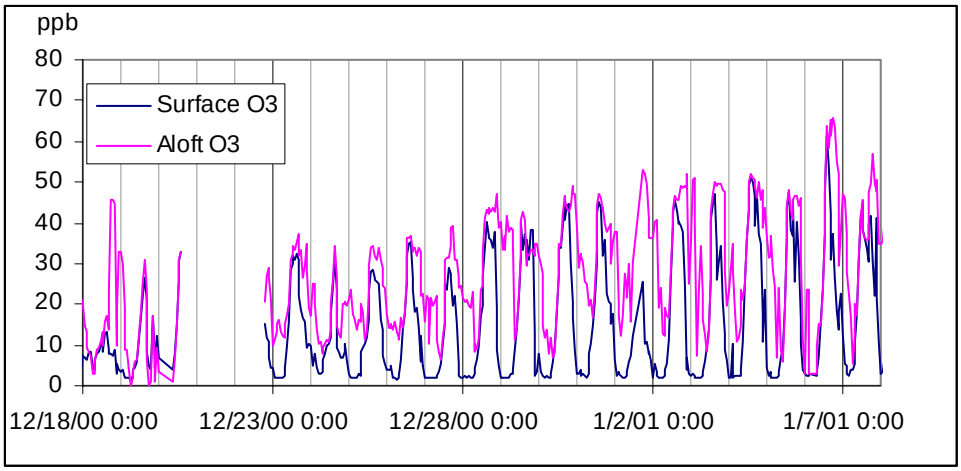


Figure 10. Surface and aloft O_3 (100 m) at Angiola tower.

The time series, average diurnal profiles, and frequency of high O_3 and PM as a function of hour of day are provided in Figure 11 and Figure 12 for the two urban areas, Bakersfield and Fresno, respectively. In the urban areas, O_3 peaks are generally lower than in the rural area. In contrast to the Angiola picture in Figure 9, daytime PM peaks are lower on many days, especially in Fresno. There is significant day-to-day variability in the diurnal profiles $PM_{2.5}$ concentrations. The diurnal profiles frequently peak at night, although secondary day-time peaks are seen on some days. The average diurnal profiles highlight these observations. The average peak O_3 is around 30 and 25 ppb in Bakersfield and Fresno, respectively. $PM_{2.5}$ concentrations tend to be higher at the urban locations compared to Angiola. The diurnal profiles for $PM_{2.5}$ show high concentrations in the late evening (8 p.m. to midnight). A secondary peak in the morning at approximately 10 a.m. is seen in the average diurnal profile in Bakersfield but not in Fresno. Due to the long term trends under the diurnal cycle, the highest 20^{th} percentile concentrations occur with only slightly higher frequency at night and can occur at virtually any hour of the day at both these locations.

Urban areas tend to have higher PM and lower O_3 than the rural site. Therefore, high O_3 and PM do not tend to occur at the same location in winter. The key difference between the urban and rural areas is the $PM_{2.5}$ profiles. The coincidental peaks of O_3 and $PM_{2.5}$ at the rural site explains why the top 20^{th} percentile concentrations occur more frequently there than at the urban sites. The urban build-up at night seems to account for the difference between the urban and rural concentrations. The implication is that there is some nighttime PM formation process that is accelerated in the urban areas, and this process superimposes on the daytime PM increase observed in Angiola to generate high PM concentrations. The accumulation of PM overwhelms the nighttime removal process that probably moderated the accumulation of $PM_{2.5}$ in Angiola.

We plot maximum 8-hour ozone concentrations and 24-hour average PM concentrations at these three sites in Figure 13 between 1 December 2000 and 8 February 2001. No correlation between O_3 and $PM_{2.5}$ is seen in the winter season; the lack of correlation is confirmed by the correlation coefficients of 0.33 at Angiola, 0.21 in Bakersfield and -0.03 in Fresno.

Daily maximum 8-hour O_3 concentrations are spatially variable, unlike in the summer when a more regional distribution is evident in Figure 8. During winter, the ozone at each site is affected by local chemistry, which includes production of O_3 and titration of O_3 that may be transported in. In Fresno and Bakersfield, peak O_3 concentrations occur consistently at 2 or 3 p.m., and the maximum 8-hour concentrations are recorded between 10 a.m. and 6 p.m. In Angiola, O_3 concentrations may remain high in the late afternoon, resulting in the maximum 8-hour concentrations recorded as late as the 1-9 p.m. period. We attribute the difference in O_3 profiles to the emissions of NO_x in urban areas and the lack of local NO_x emissions near Angiola. O_3 present during the mid-afternoon can persist later into the evening in Angiola.

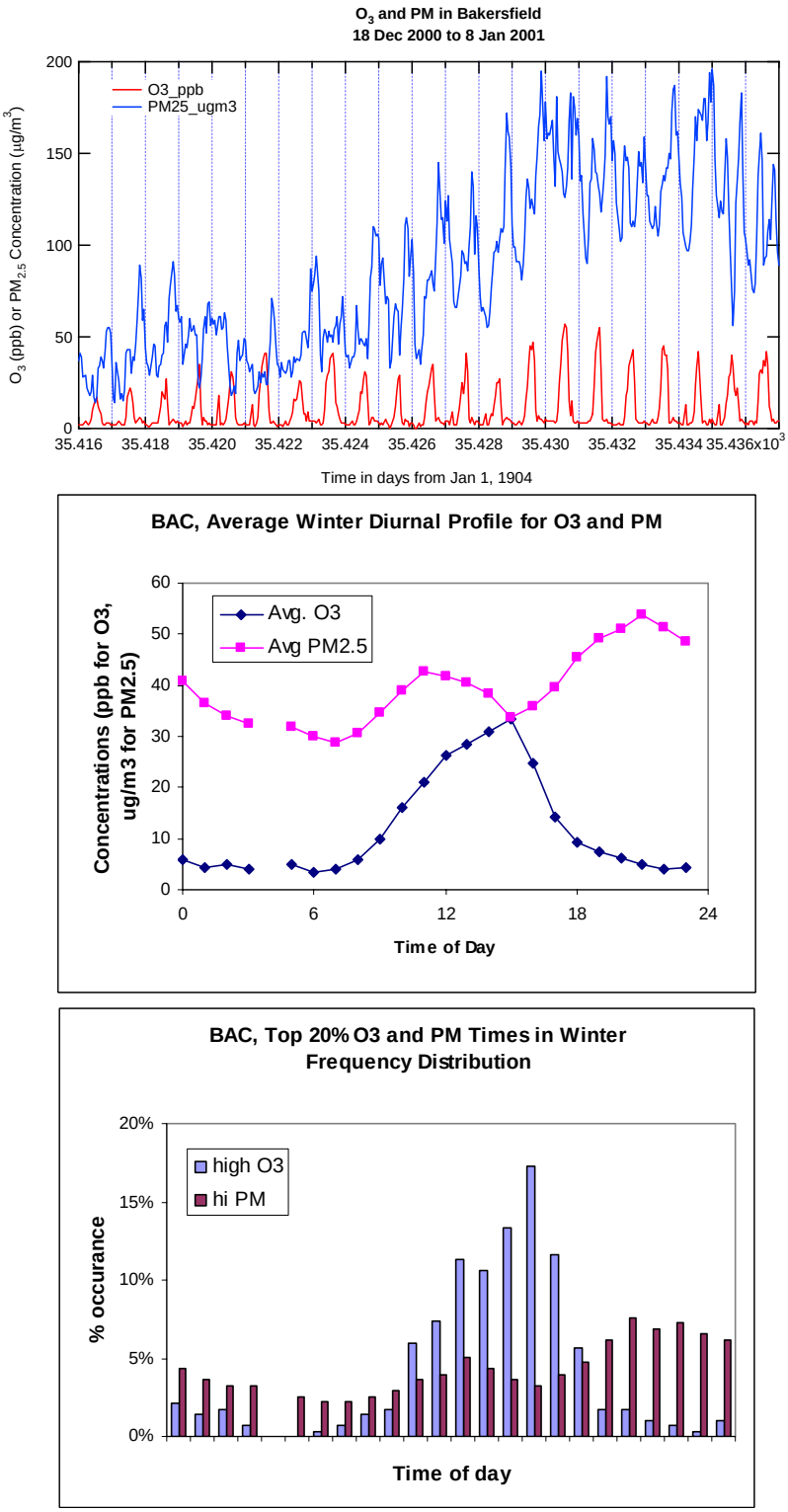


Figure 11. $PM_{2.5}$ and O_3 in Bakersfield during winter: (top) time series between 18 December 2000 and 8 January 2001, (middle) average winter diurnal profiles, and (bottom) frequency distribution by hour of top 20th percentile concentrations.

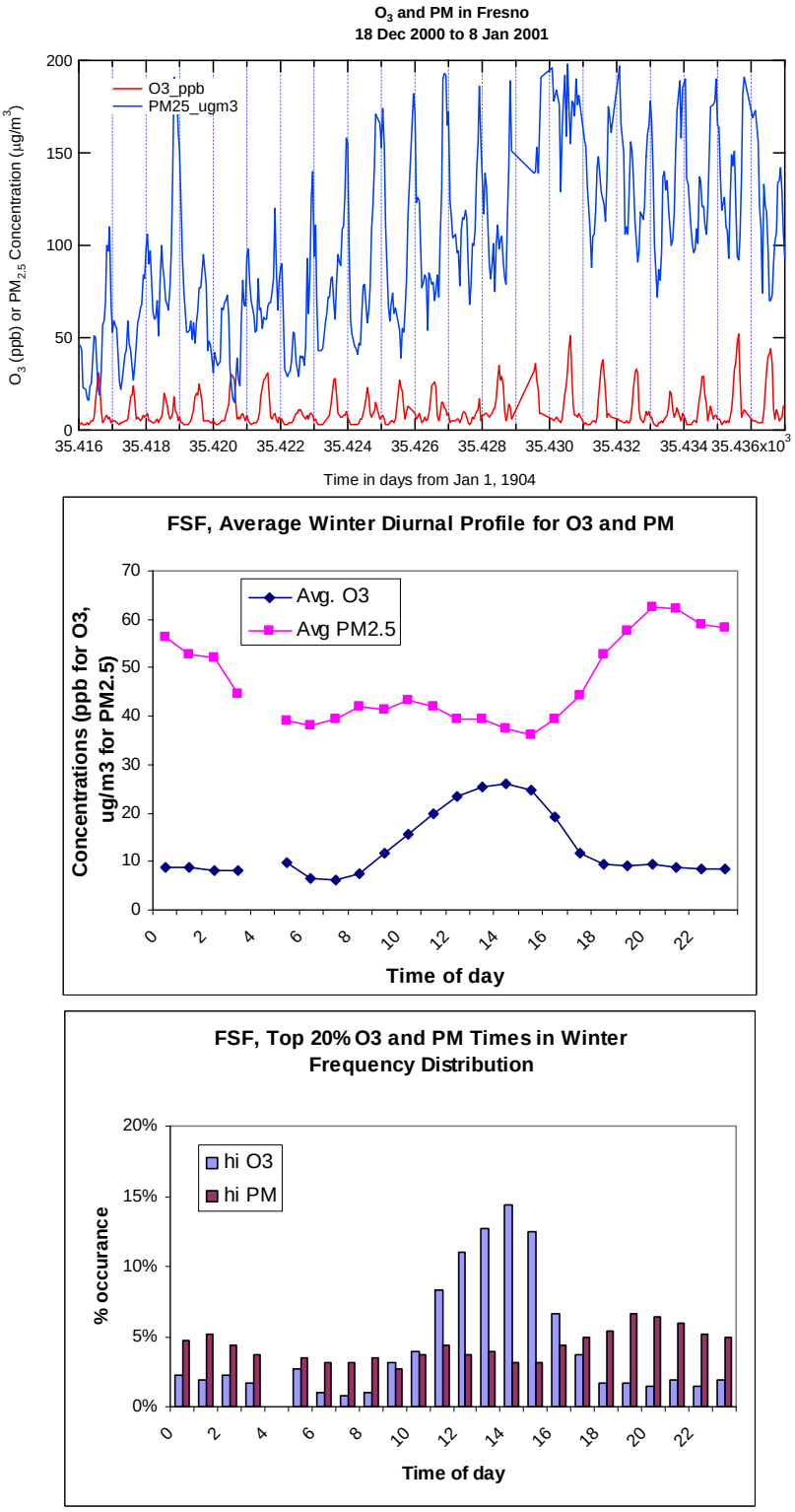


Figure 12. $PM_{2.5}$ and O_3 in Fresno during winter: (top) time series between 18 December 2000 and 8 January 2001, (middle) average winter diurnal profiles, and (bottom) frequency distribution by hour of top 20th percentile concentrations.

$PM_{2.5}$ in the San Joaquin has been shown to correlate with the synoptic mixing condition (e.g., represented by aloft (850 mb) temperature in Oakland, CA). Figure 13 shows that all three sites show the same daily trends of $PM_{2.5}$, indicating a regional distribution. Concentrations in the urban areas are higher during episodes because there seems to be a base load of $PM_{2.5}$ before the episodic buildup. In some cases, the accumulation also seems to start earlier than in Angiola.

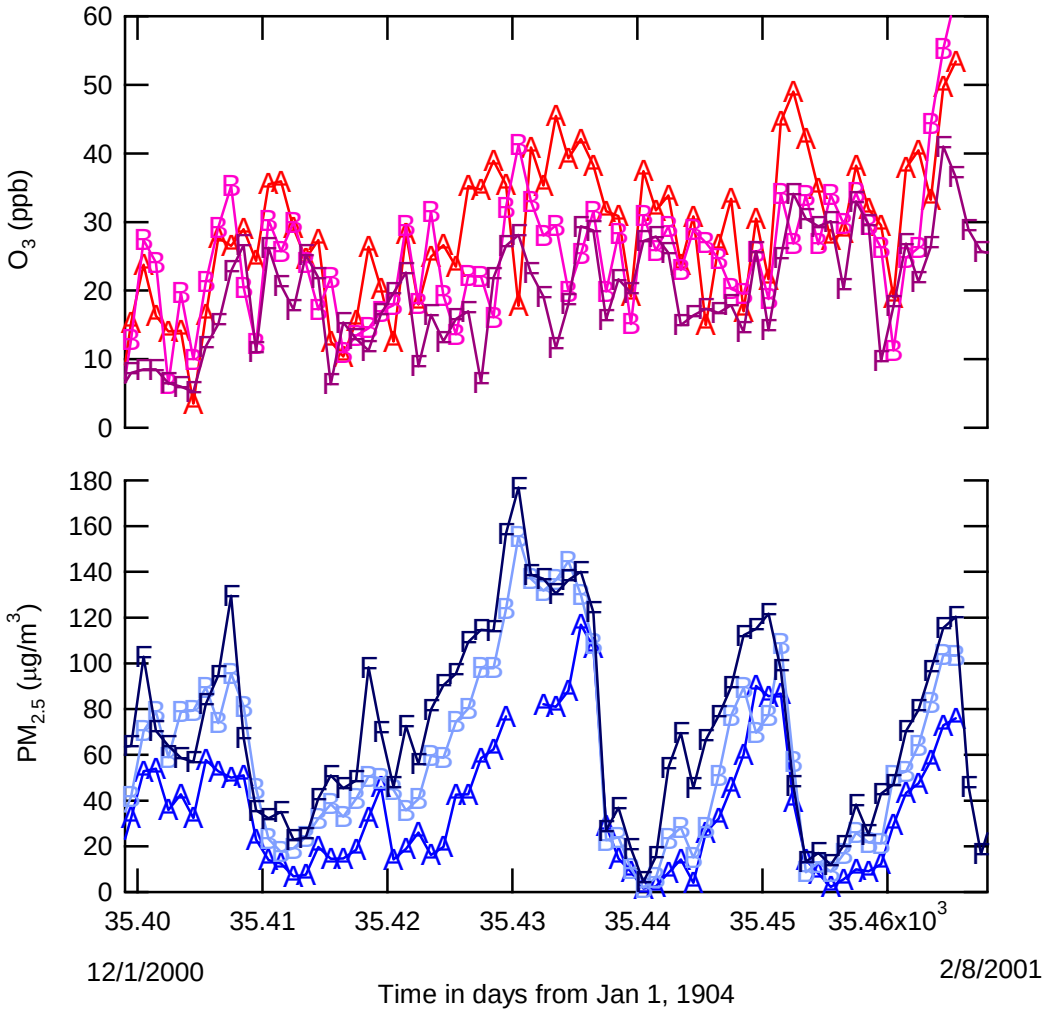


Figure 13. Daily 24-hour average $PM_{2.5}$ and maximum 8-hour average O_3 time series between 1 December 2000 and 8 February 2001 in Angiola (A), Bakersfield (B) and Fresno (F).

4. Secondary $PM_{2.5}$ Components

The average $PM_{2.5}$ composition in Angiola, Bakersfield, and Fresno is shown in Figure 14 for both summer and winter seasons. During summer, $PM_{2.5}$ concentrations are quite low and organic compounds (1.4 times organic carbon (OC)) are the largest component at all three locations, followed by ammonium sulfate. The reconstructed PM mass, assuming that both sulfate and nitrate are fully neutralized by ammonium, is typically higher than the $PM_{2.5}$ mass measurement. There are two possible reasons. First, there may not be sufficient ammonium to neutralize existing sulfate and nitrate anions. Second, the loss of volatile PM components from the mass sample may result in an underestimation of PM mass.

During winter, two components dominate: ammonium nitrate and organic compounds (1.4 times OC). $PM_{2.5}$ concentrations exceeding the 24-hour average National Ambient Air Quality Standard of 65 $\mu g/m^3$ occurred during the late fall and winter months (November through February) at Angiola, Fresno, and Bakersfield. During the late fall/winter season of 2000-2001, the NAAQS was exceeded 15 times in Fresno, 10 times in Bakersfield, and 7 times at Angiola. At Angiola, ammonium nitrate is the dominant component of $PM_{2.5}$, accounting for an average of 54 $\mu g/m^3$ $PM_{2.5}$ on exceedance days. Despite higher PM concentrations, the composition of PM on exceedance days is remarkably similar to the average winter composition at all three sites. Of the three sites, nitrate shows the largest percentage of any component at Angiola. Therefore, we look at nitrate at Angiola in greater detail in Section 4.1.

In Bakersfield, ammonium nitrate represents more than 50% of the $PM_{2.5}$ on exceedance days, but the contribution from organic compounds is higher than in Angiola. In Fresno, the ammonium nitrate contribution (35%) falls behind the organic compound contribution (45%) on exceedance days. However, OC contribution is greater than ammonium nitrate on approximately half of the exceedance days only, including 4 days during the Christmas holiday season (December 23, 26, 27, 28). Bakersfield exceeded the NAAQS on December 27 and 28 also, but Angiola showed no exceedances around the holidays. We look more closely at wintertime OC contributions in Section 4.2.

There are only 24-hour average EC and OC samples taken during the summer months. Continuous measurements for different temperature fractions of organic and total carbon are available for FSF, but not EC and OC. Therefore, ambient data are not used to estimate the characteristics of emissions; such estimates require OC/EC samples taken during periods of low photochemical reactivity. The daily OC/EC ratios are 8.2 ± 2.7 in Angiola, 6.1 ± 0.9 in Bakersfield, and 7.3 ± 1.9 in Fresno. Because of the temporal homogeneity of the 24-hour average samples, no sample was identified to be especially representative of primary emissions. The corresponding OC/EC 24-hour average ratios during winter are 5.6 ± 1.7 in Angiola, 4.5 ± 1.0 in Bakersfield, and 4.7 ± 0.7 in Fresno. The higher summer ratios are consistent with the presence of a significant amount of secondary organic compounds, although estimates of the secondary fraction could not made using the existing summer dataset.

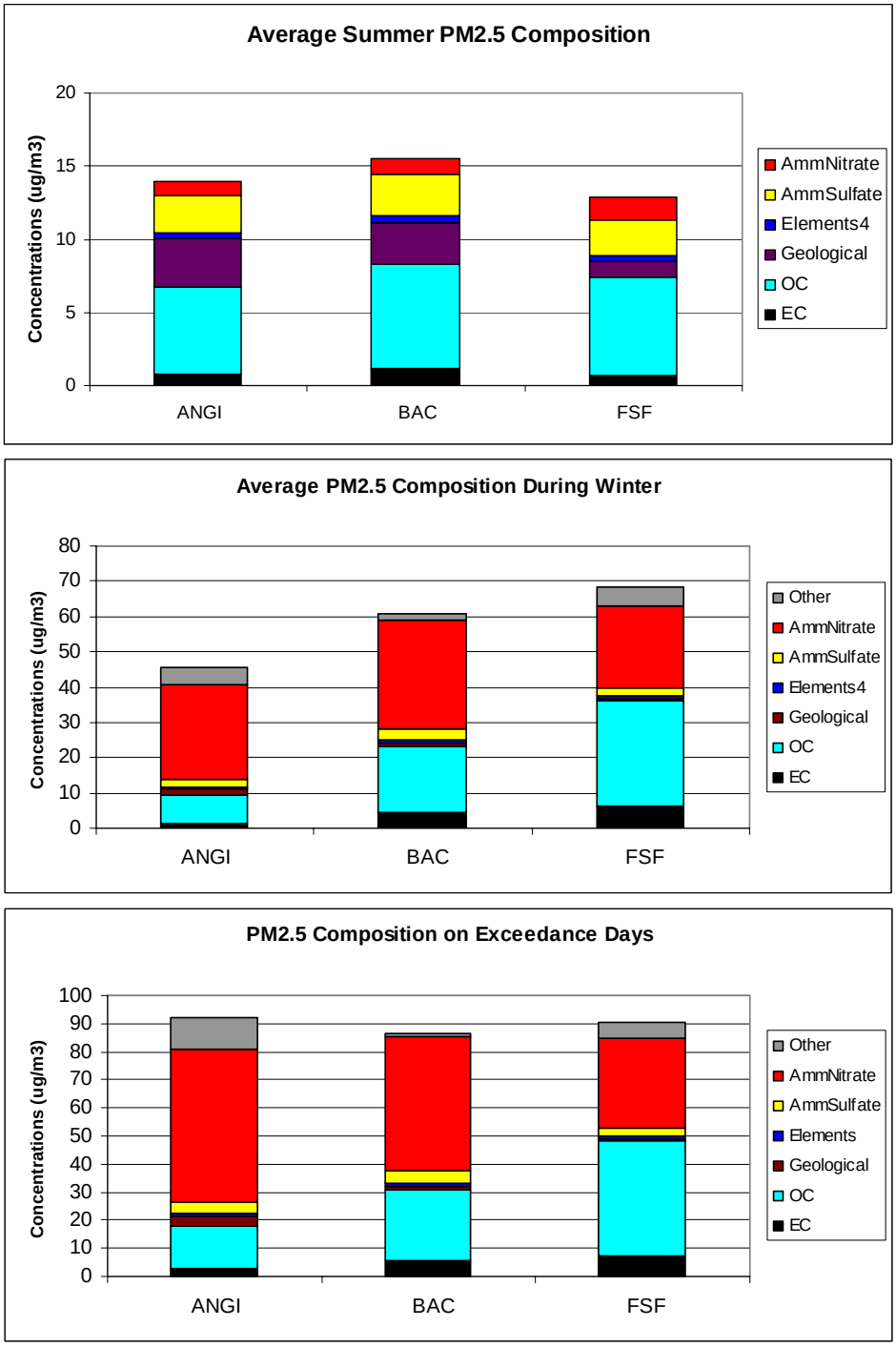


Figure 14. Composition of PM: (top) summer average, (middle) winter average, (bottom) average during exceedances days in Angiola, Bakersfield, and Fresno (data from K. Turkiewicz, December 2004)

4.1 Nitrate concentrations in Angiola during winter

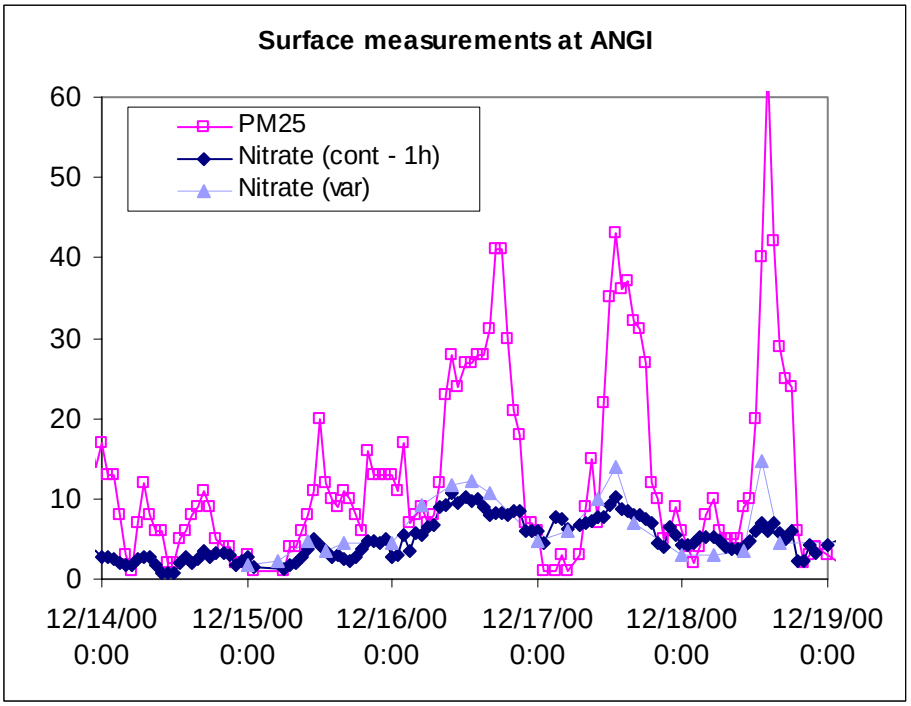
There are several potentially informative chemistry data sets in Angiola, including hourly nitrate at the surface and aloft (100 m), hourly ozone at the surface and aloft, and hourly PM at the surface. In addition, there are meteorological data at the surface and aloft to provide supplemental information. However, the analyses of these data are not without uncertainties. For example, the top panel of Figure 15 shows that the hourly data agree with the filter samples for nitrate quite well during the middle of December; however, both data sets show periods where nitrate concentrations are higher than the recorded total $PM_{2.5}$ concentrations. The bottom panel of Figure 15 shows that there are some significant data gaps in the continuous data. In addition, the agreement between the continuous nitrate measurement and the 3-8 hour filter samples deteriorated, casting some doubt on the accuracy of some of the measurements.

At the surface level, the average diurnal profiles of O_3 and nitrate during the episode days are shown in Figure 16a in Angiola. The fact that PM nitrate peaks during the day, when temperature is higher and more nitrate volatilization is likely, is consistent with a production process that occurs during the early afternoon hours.

For the Fresno supersite, the increase of $PM_{2.5}$ nitrate coincided with the rise in surface temperature in the morning and led Watson and Chow (2002) to conclude that nitrate is formed above the surface layer. However, Figure 16b shows a somewhat different average diurnal profile for nitrate in Angiola and nitrate in Fresno and Bakersfield. As discussed below, the same process may not play a large role in the profile of nitrate concentrations observed in Angiola.

As shown in Figure 17, aloft nitrate is frequently lower in concentration than surface nitrate in Angiola. There are days when the daytime peak is preceded by a nighttime peak aloft, such as on December 30, and nighttime formation of nitrate may contribute to the daytime peak. However, mid-morning increases in nitrate are not observed at ANGI in the averaged profile, as they seem to occur in Fresno and Bakersfield (see Figure 16b), and the contribution of nitrate formed aloft at night to the daytime peak may not be as consistent in Angiola as in Fresno.

Lurmann et al. (2004) argue that aloft nitrate formation takes place at Angiola based on O_3, NO, and nitrate temporal profiles, which implied the formation of nitrate via a pathway that involves the formation of NO_3 from $O_3 + NO_2$. They did not find evidence for surface nitrate production at night. Figure 17 shows that on some evenings, nitrate increases both at the surface and aloft (e.g., early morning of December 29 and 31), implying that some nighttime process can happen at the surface as well as aloft, albeit with less consistency, and despite much lower O_3 at the surface. The role of the $NO_2 + O_3$ reaction and the relative rates of aloft and surface production of nitrate cannot be verified without reliable measurements of NO_2, HNO_3, and possibly nitrate radicals.



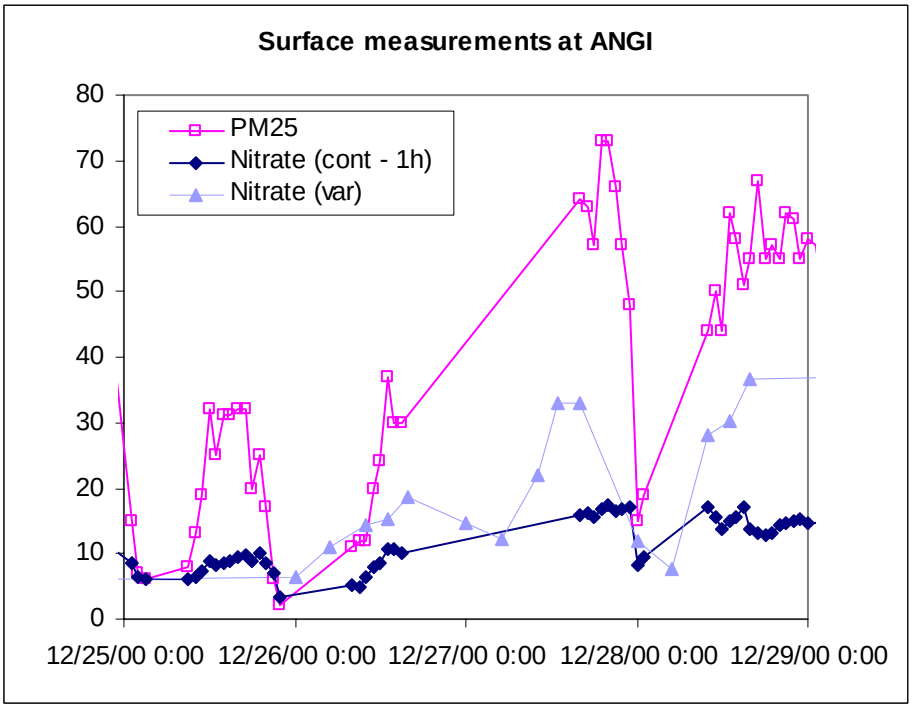
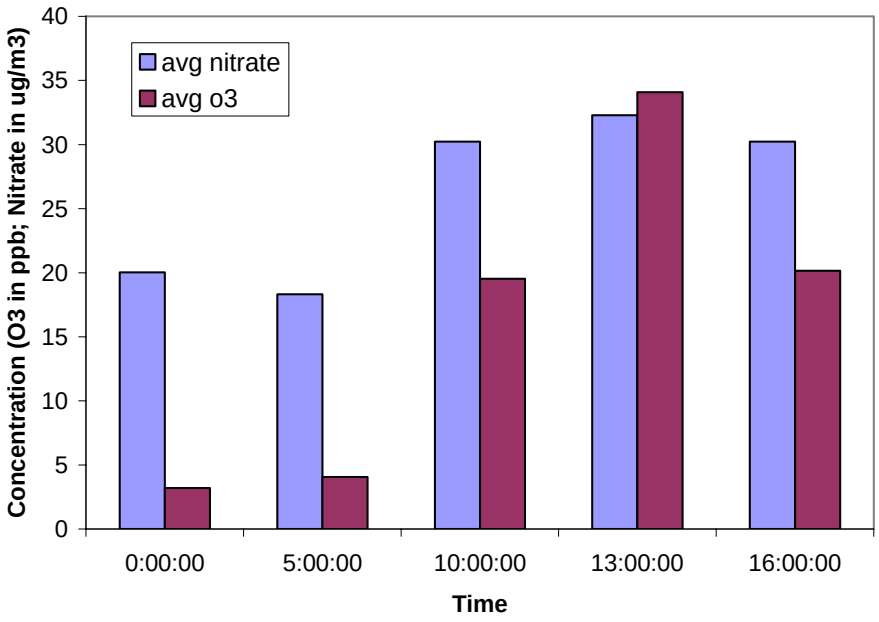


Figure 15. Time series of $PM_{2.5}$ mass and two nitrate measurements at Angiola station.

(a)



(b)

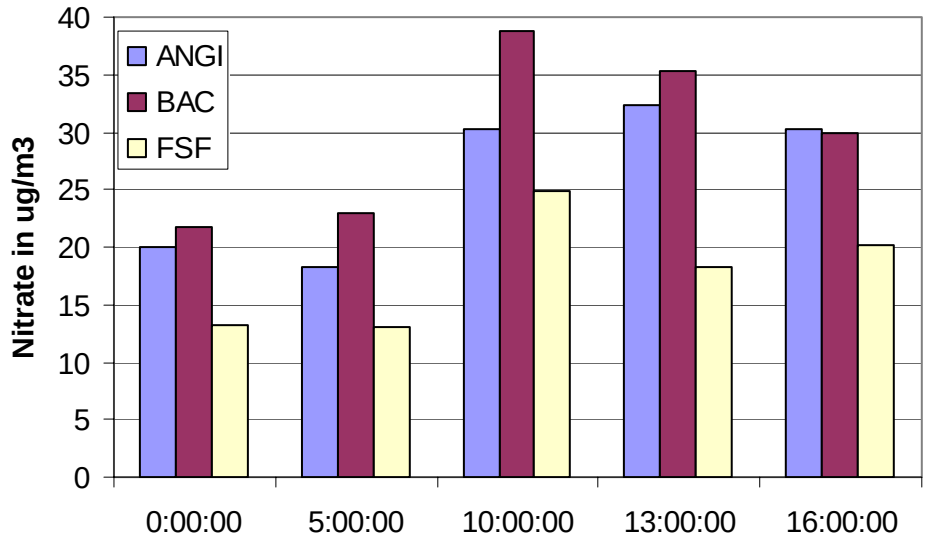


Figure 16. Average diurnal profiles of (a) nitrate and O_3 at Angiola ground station, (b) nitrate at ANGI, BAC, and FSF

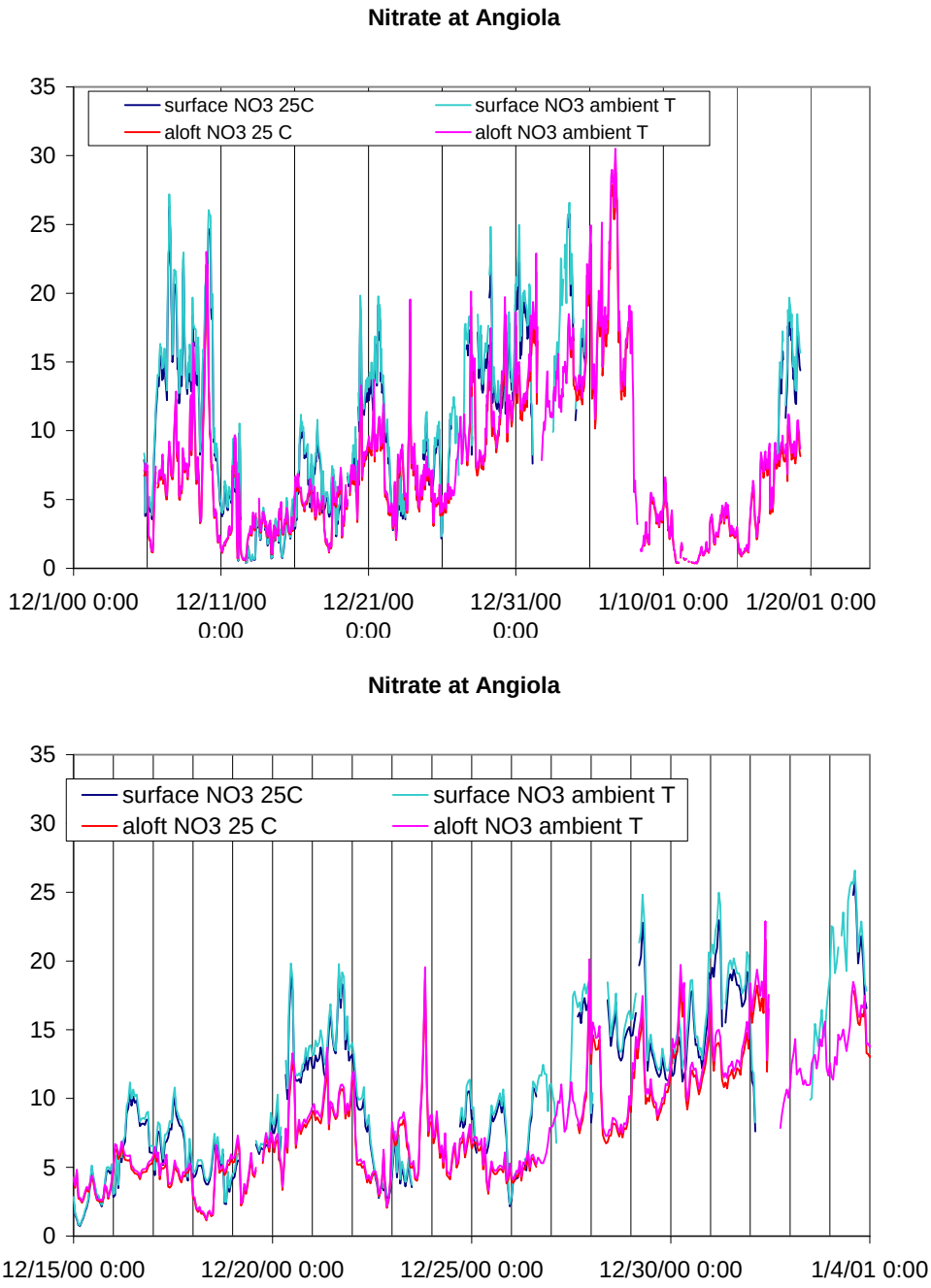


Figure 17. Time series of nitrate at surface and aloft in Angiola.

One possible explanation for the discrepancy between surface and aloft nitrate is the removal of nitrate and HNO_3 by fog, particularly at the surface, due to shallow fog that was frequently observed (J. Collett, December 2004, personal communication). On nights with fog formation, e.g., December 17, 18, 19, 25, 28, and January 2 (Figure 18), there is no accumulation of nitrate at the surface. Accumulation aloft can be seen on several of those nights. The daytime concentrations of nitrate at the surface increase with or without a corresponding increase of nitrate aloft.

The concentrations of NO_y are quite similar at the surface and aloft (Figure 19) and the concentrations of O_3 are higher aloft during the day. If NO_y represents gas-phase measurements of all nitrogen oxides, it is postulated that the formation of particulate nitrate aloft on some days may be limited by the availability of ammonia that facilitates the phase transition between gaseous HNO_3 and particulate nitrate. There are currently no ammonia measurements aloft to evaluate this assumption.

There is some evidence that chemical production of nitrate occurs at the surface during the day. It is postulated that the daytime chemical process for the production of nitrate involves OH radicals or nitrate radicals, if it persists due to slower photolysis during the wintertime. Reliable measurements of NO_2 and HNO_3 and additional measurements of nitrate radicals may be needed to evaluate the feasibility of the nitrate reaction.

4.2 Organic concentrations Fresno and Bakersfield during winter

Lurmann et al. (2004) used the OC/EC method to determine the contribution of secondary organic carbon (SOC). The ratio of OC/EC representing primary emissions was calculated to be 2.74 based on data from Bethel Island, Bakersfield, Fresno, Angiola, and Sierra Nevada Foothills when the OC/EC ratio was less than 3.5. Using this ratio, they calculated the contribution of SOC to OC to range from 7 to 48% (with an average of 16%) in Bakersfield, 15 to 38% (with an average of 20%) in Fresno, and 17 to 34% in Angiola (with an average of 26%). The highest SOC contributions were observed between 1 and 4 p.m. at all sites. In Angiola, the contribution between 4 p.m. and midnight remained quite high, whereas the contribution dropped back down in Fresno and Bakersfield.

Several assumptions are involved when applying the OC/EC method. First, the primary OC/EC ratio of 2.74 was determined based on data at all sites. The implicit assumption is that there is one characteristic ratio for emissions at all sites, thus ignoring the geographic variability of the emission sources. Second, it is also conceivable that the amount of primary and secondary OC vary on a day-by-day basis. For example, holiday emissions have been postulated to be dominated by biomass burning (fireplaces), which may not be the dominant source during warmer days. The following analysis provides alternative estimates of the amount of SOC using geographically variable OC/EC ratios and provide some examples of how temporally variable the estimates of the primary and secondary OC can be.

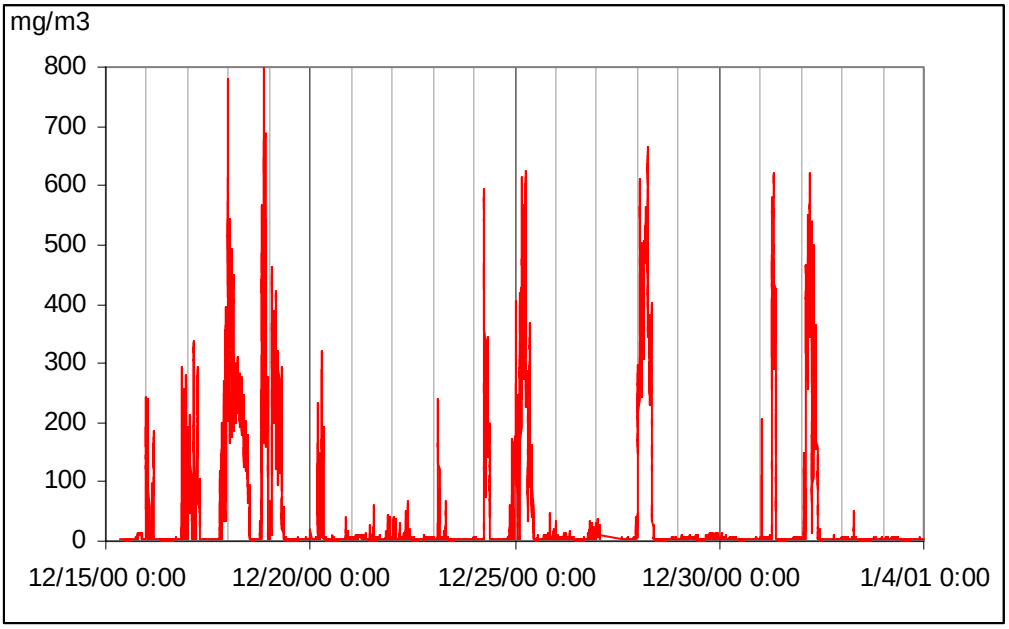


Figure 18. Fog liquid water content at Angiola surface station.

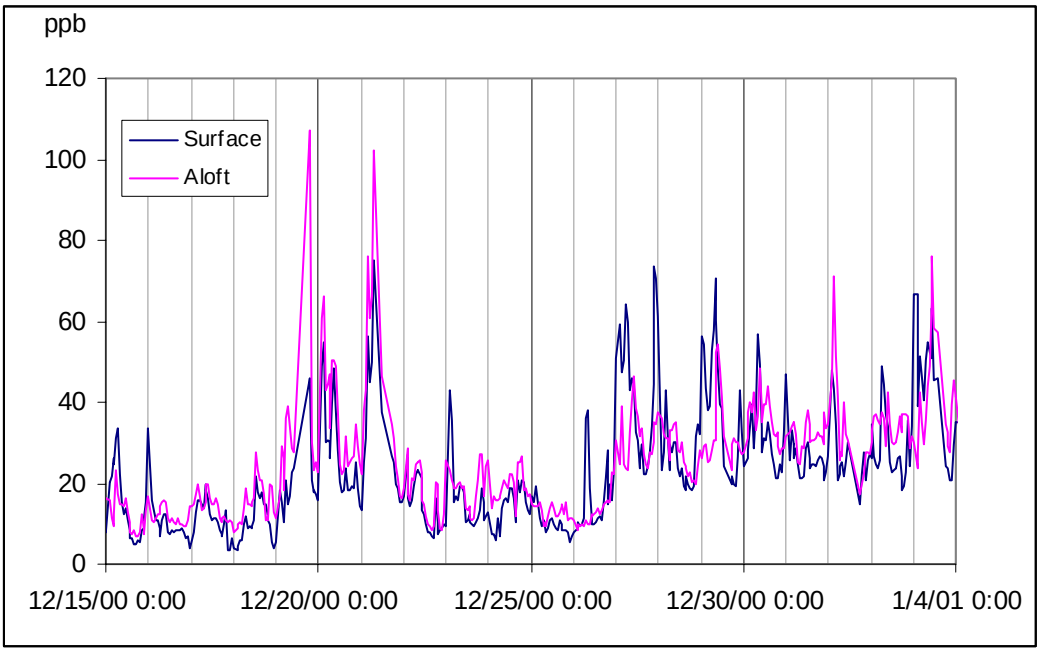


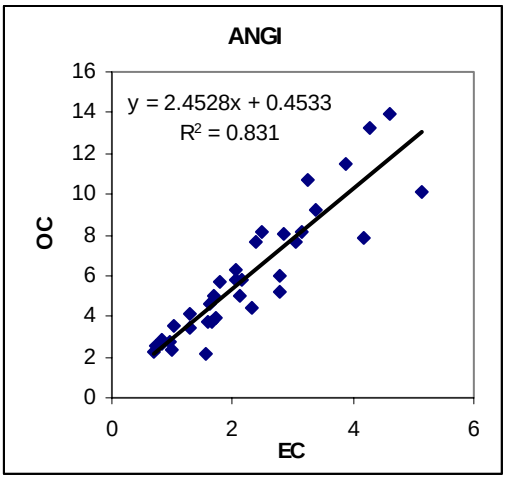
Figure 19. NOy concentrations at Angiola Tower at surface and 100 m height.

Figure 20 shows the scatter plots of OC vs. EC when the ratios are less than 3.5 for Angiola, Bakersfield, and Fresno, and for all three locations together. There are over thirty samples at each location that have OC/EC ratios of 3.5 or less. Several interesting observations are made based on Figure 20. The Fresno data, with a tight correlation between OC and EC and a small intercept, is closest to the expectation that OC and EC originates from the same sources, and can be related using a simple ratio of 2.9. In Bakersfield, the good correlation between OC and EC implies that both concentrations are driven by local emissions when the ratio is low. However, there is a fairly significant intercept of 2.2 $\mu g/m^3$ of OC, which can be interpreted as a background of OC (unrelated to EC) concentrations that can be primary or secondary, local or regional. In Angiola, the intercept is small, but the correlation is not as strong as in the urban areas. This may be an indication that Angiola is affected by different source areas with slightly different OC/EC characteristics on different days. When forced through zero, the OC/EC ratios are 2.61, 2.55, and 2.95 in Angiola, Bakersfield, and Fresno, respectively. These ratios are used to provide an alternative estimate of the contribution of secondary compounds at these sites.

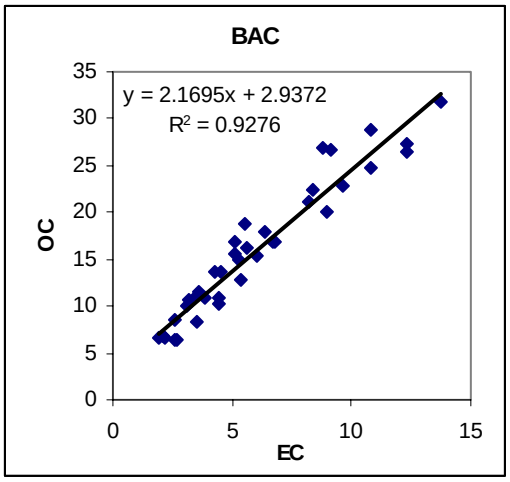
In Angiola, the ratio of 2.61 used in the new estimates results in lower OC associated with direct emissions and larger amounts of OC assigned to secondary compounds than Lurmann et al's ratio of 2.74. The average diurnal profile of primary organic carbon (POC) and SOC are shown in Figure 21. Because the amount of EC is fairly constant as a function of time, the POC fluctuates within a small range of 4.3 (0 to 10 a.m.) to 5.0 $\mu g/m^3$ (1 to 4 p.m.). SOC ranges from 0.8 (0 to 5 a.m.) to 3.8 $\mu g/m^3$ (1 to 4 p.m.), reflecting photochemical production in the afternoon. The fraction of SOC in OC ranges from 15 to 44%, averaging 32% (time weighted average SOC / (time weighted average POC + time weighted average SOC).

The primary OC/EC ratio (2.55) used to provide the alternative estimates in Bakersfield also results in higher SOC estimates than Lurmann et al. (2004), as shown in Figure 21. POC ranges from 5.2 (1 to 3 p.m.) to 15.2 $\mu g/m^3$ (4 p.m. to midnight). Low mid-afternoon concentrations reflect dilution of primary emissions. SOC ranges from 1.0 (5 to 10 a.m.) to 5.2 $\mu g/m^3$ (1 to 4 p.m.), reflecting photochemical production in the afternoon. The fraction of SOC in OC ranges from 8 to 50%, averaging 17%.

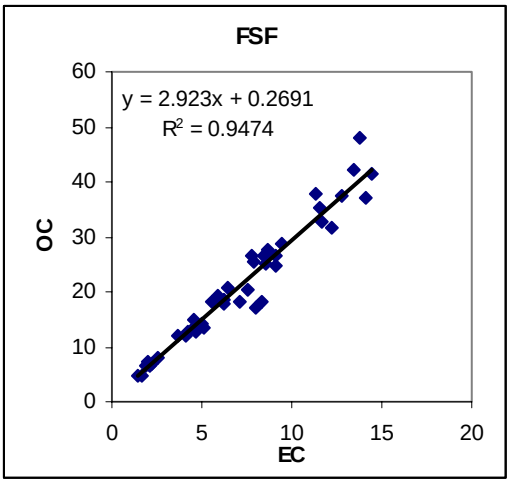
The primary OC/EC ratio (2.95) used to provide the alternative estimates in Fresno also results in higher POC estimates and lower SOC than Lurmann et al. (2004), as shown in Figure 21. POC ranges from 6.2 (1 to 3 p.m.) to 27.6 $\mu g/m^3$ (4 p.m. to midnight) in the average diurnal profile. Low mid-afternoon concentrations reflect dilution of primary emissions. SOC ranges from 0.9 (5 to 10 a.m.) to 3.8 $\mu g/m^3$ (4 p.m. to midnight). The photochemical activity signal in the afternoon is absent in the absolute concentration profile, replaced by high SOC estimates when OC concentrations are high (see Figure 22). The fraction of SOC in OC ranges from 5 to 31% (between 1 and 4 p.m., indicative of photochemistry), averaging 13%.



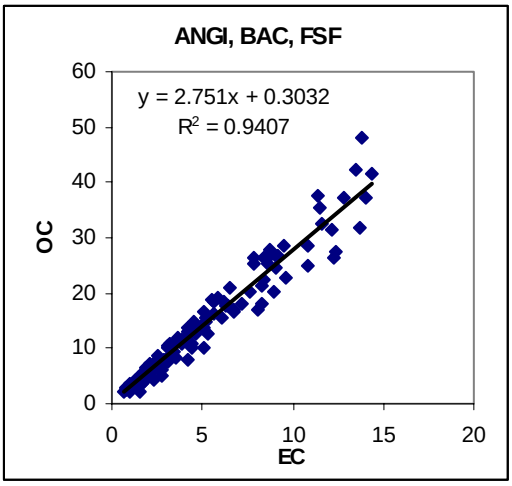
ANGI: y = 2.61 x; R^2 = 0.83



BAC: y = 2.55 x; R^2 = 0.89



FSF: y = 2.95 x; R^2 = 0.95



3 sites: y = 2.79 x; R^2 = 0.94

Figure 20. OC vs. EC when the ratio is less than 3.5 for Angiola (top left), Bakersfield (top right), Fresno (bottom left) and all three sites together (bottom right).

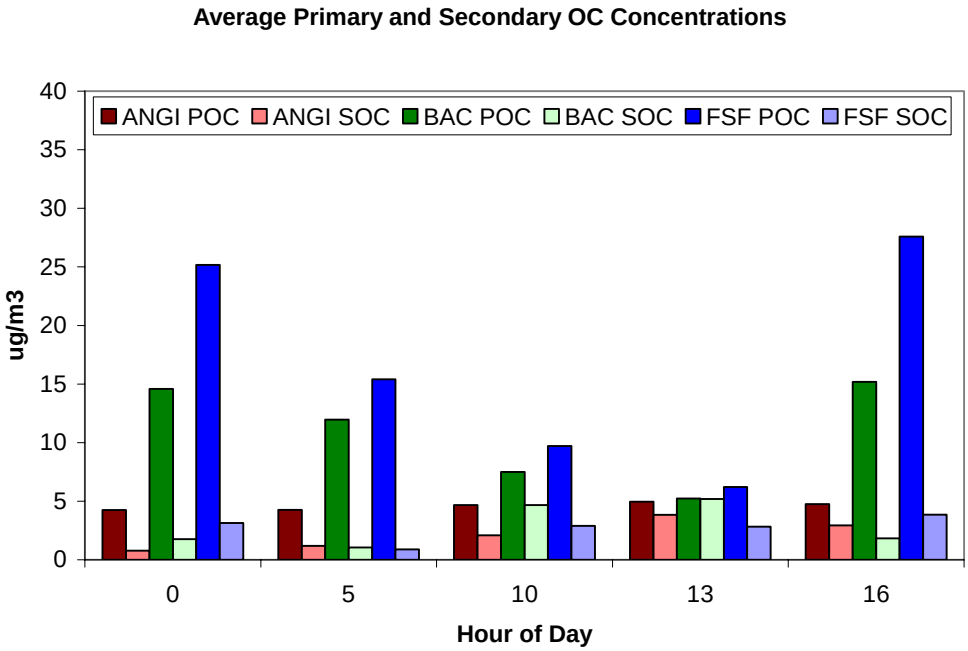


Figure 21. Primary and secondary OC estimates group by hour of day using location-specific primary OC/EC ratios.

Figure 22 shows the average diurnal profile of OC and EC at the three sites on all episode days and on exceedance days, together with the associated OC/EC ratios. At all three sites, both EC and OC concentrations are higher on exceedance days than on episode days. Whereas the two urban areas show small changes in the OC/EC ratios as a function of time, the OC/EC ratios are generally lower in Angiola on exceedance days compared to all episode days, indicating a stronger influence of primary emissions. The diurnal average estimates of primary and secondary OC are shown in Figure 23 for the exceedance days. In Angiola, the average primary contribution is 7.1 $\mu g/m^3$, the secondary contribution is 1.4 $\mu g/m^3$, which is lower than on all 15 episode days. The secondary contribution represents 16% of total OC, and is significantly lower than the average contribution. In Bakersfield, the primary contribution is estimated to be 17.3 $\mu g/m^3$ on average on exceedance days, while the secondary contribution remains the same as before, at 2.3 $\mu g/m^3$. As a result, the contribution of SOC is also lower on exceedance days than on all episode days. In Fresno, both primary and secondary OC are estimated to increase in concentrations on exceedance days. The contribution of SOC is the same as on the 15 episode days, averaging 13%.

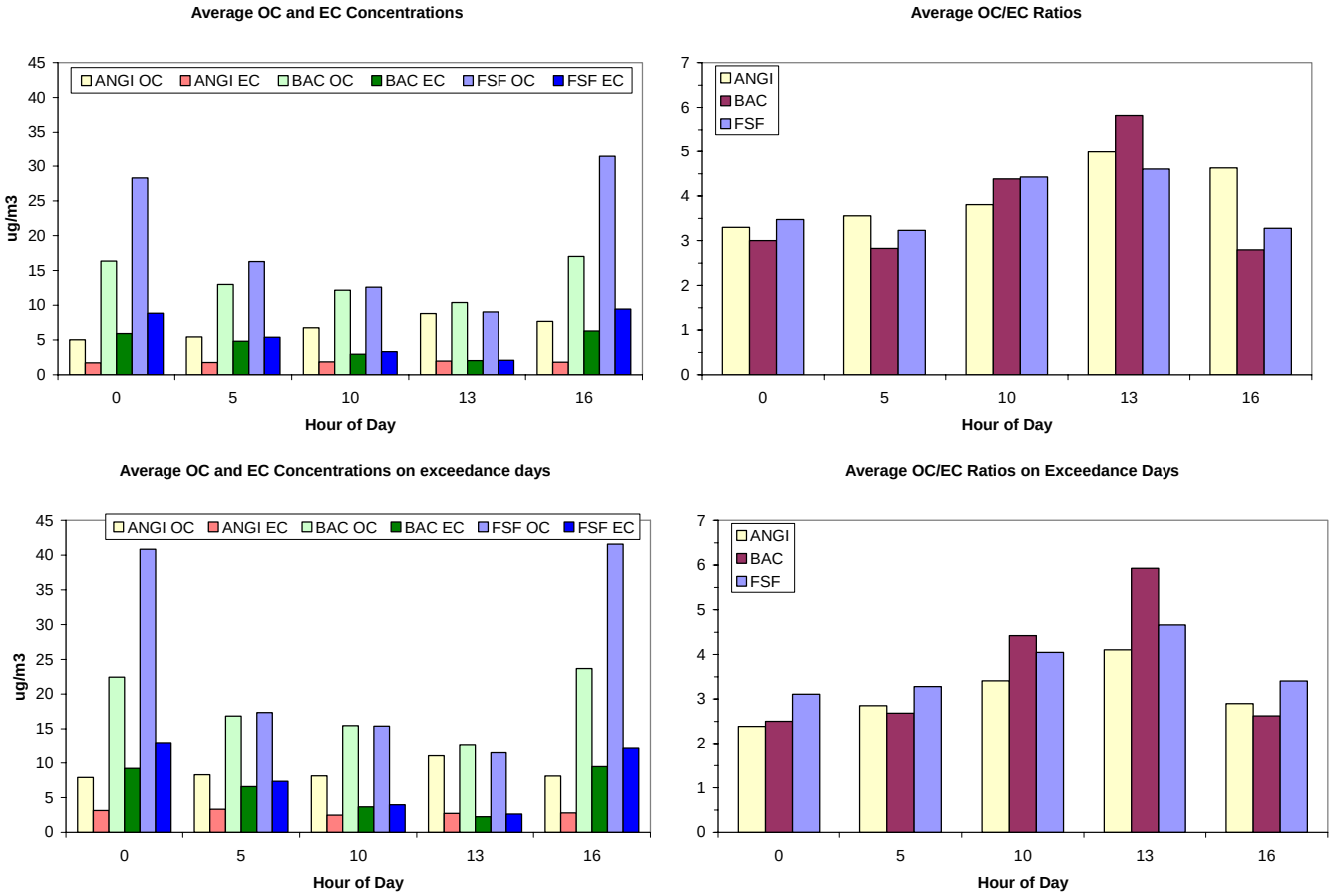


Figure 22. Average diurnal profiles of OC and EC measurements and OC/EC ratios on all episode days (top) and on exceedance days (bottom).

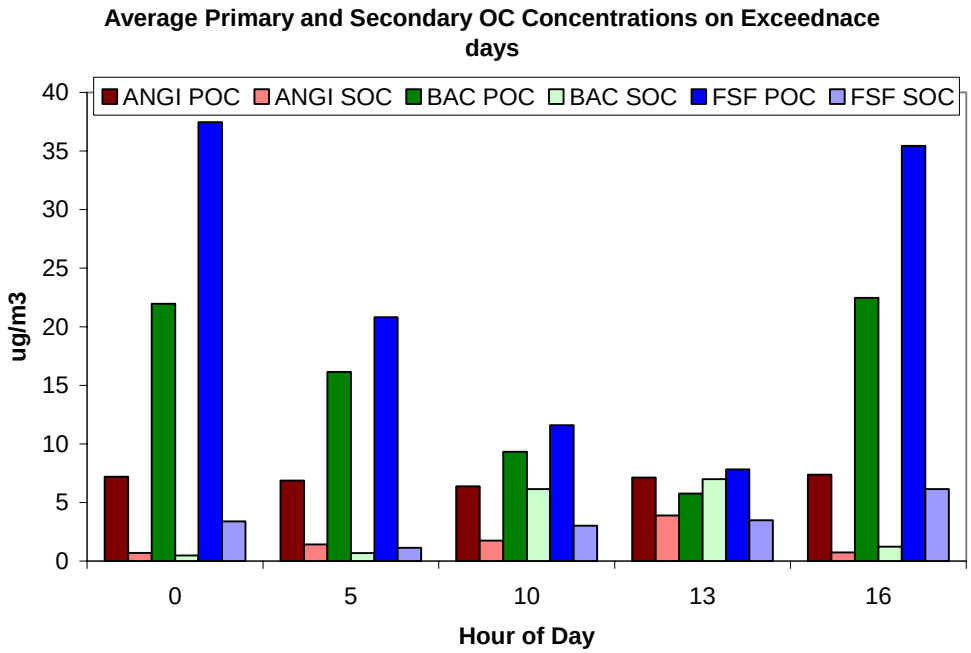


Figure 23. Primary and secondary OC estimates grouped by hour of day using location-specific primary OC/EC ratios.

5. Summary and Conclusions

5.1 High O_3 vs. High $PM_{2.5}$

On an annual basis, O_3 and $PM_{2.5}$ do not correlate. Any relationship is obscured by the seasonal behavior of these pollutants, i.e., O_3 being high in the summer and $PM_{2.5}$ being high in the winter. When the dataset is stratified by season, seasonal and geographical differences in the relationship between O_3 and $PM_{2.5}$ are revealed.

- In Angiola, the rural site, top 20^{th} percentile O_3 and $PM_{2.5}$ concentrations occur simultaneously most frequently in winter
- In Bakersfield and Fresno, top 20^{th} percentile O_3 and $PM_{2.5}$ concentrations occur simultaneously most frequently in summer

O_3 and $PM_{2.5}$ show very different diurnal behaviors. The 24-hour cycle of O_3 is very pronounced in both the winter and summer time series at all three locations. $PM_{2.5}$ fluctuations show no discernable cycles in the summer. During winter, $PM_{2.5}$ shows a lot of structure: daily cycles are seen on some days to superimpose on a longer term build-up. However, there is no consistent shape to the diurnal cycle of $PM_{2.5}$ as there is for O_3. O_3 is removed every evening by chemical titration and builds up from a low concentration in the early morning. $PM_{2.5}$ does not show a consistent removal process. While PM concentrations decrease during some hours of the day, long-term accumulation is observed during winter episodes.

During winter, high concentrations of $PM_{2.5}$ and O_3 occur together in Angiola because daily peak concentrations for both species occur during the day on many days with high PM concentrations. The diurnal cycles of winter PM and O_3 at the urban sites show a phase difference between these two pollutants.

During summer, high concentrations of $PM_{2.5}$ and O_3 occur together in Fresno and Bakersfield because there is a stronger tendency for O_3 and $PM_{2.5}$ to build up together during an episode. The long-term trends, calculated using 24-hour average $PM_{2.5}$ and daily maximum 8-hour average O_3 concentrations, show stronger correlations at the urban sites than at the rural site.

5.2 $PM_{2.5}$ Composition

In Angiola, nitrate is the dominant component of winter $PM_{2.5}$ and the daytime peaks of $PM_{2.5}$ are caused by daytime peaks in $PM_{2.5}$ nitrate concentrations. Since daytime conditions are comparatively less favorable for nitrate to partition into the particulate phase, peak concentrations during the 1 to 4 p.m. period are strongly indicative of a daytime chemical process occurring at this site. Nighttime drops in nitrate concentrations may be due to removal by fog. There is some indication of nitrate formation aloft, but the contribution of aloft nitrate to surface observations at this site is not readily observed as a consistent morning increase of surface nitrate is lacking in the Angiola data.

The difference in the nitrate diurnal profiles in Angiola and at the urban sites indicates that the dominant processes contributing to the observed surface nitrate concentrations may be different at urban and rural sites. Transport from aloft was assumed by Watson and Chow (2004) to account for a morning increase in nitrate concentrations at the Fresno supersite. A more complete understanding of the formation of nitrate at various locations awaits reliable and simultaneous measurements of NO_2, HNO_3 (maybe NO_3 radicals) and particulate nitrate.

In Fresno, organic compounds dominate the $PM_{2.5}$ concentrations in winter. Organic compounds concentrations peak at night, coincidental with $PM_{2.5}$ mass concentrations. Since organic compounds are more concentrated around urban areas than rural areas, it is inferred that urban-scale nighttime emissions, e.g., from residential wood burning, are a major source of organic compounds in urban areas.

5.3 Contribution of Photochemical End Products to $PM_{2.5}$

Secondary compounds that are produced from photochemical reactions include ammonium nitrate, ammonium sulfate, and a portion of the organic compounds. The estimated average concentrations of ammonium nitrate, sulfate, and SOC for the rural and urban sites are listed in Table 4 for the winter season. The estimates of SOC are based on the OC/EC method, with a site-specific minimum OC/EC ratio that is calculated to represent the source mixture at each site, because urban sites are postulated to be affected by local, rather than regional, emissions. The primary ratio is estimated to be 13% higher in Fresno than in Bakersfield. There is some evidence that the contribution of POC in Angiola is higher on exceedance days.

Photochemical end products account for more than half of $PM_{2.5}$ in Angiola and Bakersfield but for less than half of $PM_{2.5}$ n Fresno.

For the summer season, estimates of SOC cannot be made due to a lack of processed time-resolved OC and EC measurements at all sites that correspond to the organic and elemental carbon data used in winter. (Organic and total carbon temperature fractions are available at FSF). The higher OC/EC ratios during summer are consistent with higher contributions from SOC, although time-resolved measurements of OC and EC at both urban and rural sites will be needed to evaluate the contributions of SOC.

The formation of ammonium nitrate in the summer is limited (1.0 $\mu g/m^3$ (7%) in Angiola, 1.1 $\mu g/m^3$ (7%) in Bakersfield, and 1.6 $\mu g/m^3$ (12%) in Fresno) because higher temperatures favor the gaseous form of nitrate over the particulate form. Ammonium sulfate is the second most abundant PM species, although the assumption that sulfate is completely neutralized should be verified. If ammonium sulfate is assumed, the concentration is 2.5 $\mu g/m^3$ in Angiola (18%) and Fresno (19%) and 2.8 $\mu g/m^3$ (18%) in Bakersfield.

Table 4. Concentration ($\mu g/m^3$) of ammonium nitrate, ammonium sulfate, and secondary organic carbon during winter at Angiola, Bakersfield, and Fresno.

Compound	**Angiola**	**Bakersfield**	**Fresno**
Ammonium nitrate	26.9	30.7	23.1
Ammonium sulfate	2.3	3.1	2.1
Secondary OC	2.1	2.4	2.8
$PM_{2.5}$	56.3	58.9	67.3

References:

Lurmann, F.W., S.G. Brown, M.C. McCarthy, P.T. Roberts, 2004. Processes influencing secondary aerosol formation in the San Joaquin Valley during Winter, Manuscript

Watson, J.G. and J.C. Chow, 2002. A wintertime $PM_{2.5}$ episode at the Fresno, CA, supersite, *Atmos. Environ.* **36,** 465-475.